ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

BIODIESEL COST ANALYSIS IN SPAIN AND TURKEY

M.Sc. Thesis by
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Department : Chemical Engineering

Programme : Chemical Engineering

AUGUST 2009

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ABREVIATIONS

ASTM **:** Amerian Society of Testing and Material
CEPCI : Chemical Engineering Plant Cost Index
CN : Cetane Number
CP : Cloud Point
DME : Dimethyl Ether
EN : European Norms
ETBE **:** Ethyl Tert-Buthyl Ether
EU **:** European Union
FAEE : Fatty Acid Ethyl Ester
FAME : Fatty Acid Methyl Ester
FCV **:** Fuel Cell Vehicles
FTL **:** Fischer-Tropsch Liquids
GJ : Giga Joule
GW **:** Giga Watt
GWh **:** Giga Watt hour
kPa : Kilo Pascal
kWh : Kilo Watt hour
LPG : Liquefied Petroleum Gas
MJ : Mega Joule
M Toe **:** Million Tonnes of oil equivalent
MW **:** Mega Watt
PP : Pour Point
ppm : Parts per million
t **:** tonne
TBHQ **:** Tertiary Butyl Hydroquinone
TG : Triglyceride
TJ **:** Tera Joule
UK : United Kingdom
USA **:** United States of America
wt : Weight
y : year

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BIODIESEL COST ANALYSIS IN SPAIN AND TURKEY

SUMMARY

By 2030, the world's population is expected to reach 8 billion, and as the population grows, more energy is required to produce the basic needs of people. New sources of energy are needed, an energy that is more practical to use in the same way that it is safer, renewable, available and of course affordable. Renewable energy resources can be classified as; solar energy, wind energy, water power (hydropower, geothermal energy, wave energy), biomass energy and hydrogen energy. From these resources, biomass is a renewable, environmentally friendly strategic energy resource, which can be produced every where and has influence on socio-economic development, and also can be a resource for electricity and transportation fuels production. From the biomass energy technologies, biodiesel is one of the candidates of this needed energy because of its abundance and potential source in the country. Biodiesel is a clean-burning diesel replacement fuel that can be used in compression-ignition engines, and which is manufactured from virgin vegetable oils, animal fats, algaes, and waste cooking oils through the process of transesterification reaction. For industrial-scale biodiesel production around the world, canola oil, sunflower oil, soybean oil and used cooking oil are used as an oil feedstock, methanol is used as an alcohol and alkaline catalysts (sodium or potassium hydroxide) are used as catalyst choices. In this project, the biodiesel transesterification production process in large-scale of a plant with an annual production of 8.000 tonnes of this biofuel was studied, using canola oil, methanol and sodium hydroxide as the main substances. The flowsheet of the process was designed and the mass balance was done. Once this step was finished, the economical assessment of two plants with the same characteristics as the one designed, one in Spain and the other one in Turkey, was carried out. Results showed that in both countries a solution is needed in order to make the process profitable: cheaper feedstocks, new technologies, or new policies, incentives, subsidies or tariffs from the government.

İSPANYA'DA VE TÜRKİYE'DE BİYODİZEL MALİYET ANALİZİ

ÖZET

2030 yılında dünya nüfusunun 8 milyar olarak nüfusun çoğalması insanların temel ihtiyaçlarının üretimi için daha fazla enerjiye ihtiyaç duyulacaktır. Yeni enerji kaynaklarına ihtiyaç var olup, bir enerji kaynağının daha genel kullanımı için enerji hem güvenli, hem yenilenebilir, hem ulaşlabilir, hem de satın alınabilir olmalıdır. Yenilenebilir enerji kaynakları; Güneş enerjisi, rüzgar enerjisi, su gücü (hidro enerji, jeotarmal enerji, dalga enerjisi), biyokütle enerjisi ve hidrojen enerjisi olarak sınıflandırılabilir. Bu kaynakların arasında, biyokütle yenilenebilir, çevre ile dost bir stratejik enerji kaynağı olup, heryerde üretilebilir ve sosyo ekonomik geliştirme etkisine sahip olup aynı zamanda da elektrik üretimi ve ulaşım için yakıt üretim kaynağıdır. Biyokütle enerji teknolojilerinden, biyodizel bu enerji ihtiyacını karşılamada bol bulunması ve ülkede potansiyel kaynak olması nedeniyle adaylardan birisidir. Biyodizel basınçlı – içten yanmalı motorlarda kullanılabilen, yağlı tohum bitkilerinden, hayvansal yağlardan, alglerden, atık kızartma yağlarından transesterifikasyon süreci ile üretilebilen, motorinin yerini alabilme özelliğinde, temiz bir dizel alternatifidir. Dünyada endüstriye çerçevede biyodizel üretimi için, kanola yağı, soyafasulyesi yağı ve kullanılmış kızartma yağları yağ kaynağı olarak, metanol alkol olarak ve alkali katalizör (sodyum veya potasyum hidroksit) katalizör kaynağı olarak kullanılır. Bu projede, geniş bitki ölçeğinin, biyodizel transesterifikasyon üretim sürecinde, temel içerik olarak kanola yağı, metanol ve sodyum hidroksit kullanılarak, bu biyodizelin yıllık sekizbin ton üretimi ile çalışıldı. Üretim şeması süreci dizayn edildi ve kütle dengesi sağlandı. Öncelikle İspanya'dan ve Türkiye'den bir birlerine benzer karakteristikleri olan ekonomik olarak iki bitki üzerinde çalışıldı. Sonuçlar, her iki ülkede de sürecin karlı olmasının; daha ucuz tohum stoğuna, yeni teknolojilere veya yeni düzenlemelere, yeni teşviklere, devlet teşviklerine veya destekleyici vergilere bağlı olduğunu gösterdi.

1. INTRODUCTION

Energy is a key ingredient in the quality of our lives. We are dependent on energy for living our everyday life: it powers our industry, transport, home, etc. It provides us with heat and electricity daily. Energy demand will increase significantly in the future: by the year 2050, world-wide energy demand is projected to be at least two times more than the current level. For this and other reasons, energy supply must be sustainable and diverse and should be used more efficiently. All forms of energy are stored in different ways and these sources can be classified in different groups, but the most common are:

- Renewable, an energy source that can be replenished in a short period of time.
- Non-renewable, an energy source that we are using up and cannot recreate in a short period of time. It includes coal, gas and oil.

Renewable energy sources include:

- Solar energy, which comes from the sun and can be turned into electricity through photovoltaic cells, and heat through solar thermal systems.
- Wind, which can pump water by the use of conventional mills or produce electricity through a wind turbine.
- Geothermal energy, which use the temperature from inside the earth to produce electricity.
- Biomass, which can be combusted to generate electricity or heat, or processed to produce biofuels, such as biodiesel.
- Hydro power and ocean energy from water, which produce electricity through hydro electric, wave and tidal systems.

From the beginning of history up to the industrial revolution in the 18th century, the use of energy relied only on muscular and biomass sources. Most work was provided by manual labor and animals, while the biomass, mainly wood, provided for heating and cooking energy needs. Other sources of energy, such as windmills and watermills were present but their overall contribution was marginal.

By the mid 19th century, the industrial revolution brought a major shift in energy sources with the usage of coal, mainly for steam engines, but increasingly for power plants. As the 20th century began, the major reliance was on coal, but a gradual shift towards higher energy content sources like oil began. This second major shift inaugurated the era of the internal combustion engine and of oil-powered ships.

In the late 20th century, the emphasis on petroleum products as the main provider of energy reached the point where the world economy highly depends on the internal combustion engine and supporting industries. As its level of technical expertise increased, mankind was able to tap on more efficient sources of fossil fuels, mainly natural gas, and energy released by matter itself like nuclear fission.

The 21st century will be characterized by major shifts in energy sources with a gradual obsolescence of polluting fossil fuels, like coal and oil, for more efficient fossil fuels such as natural gas, although there may be substantial clean coal technology potential. Nuclear energy, if nuclear fusion becomes commercially possible, may also play a significant role. A very important change in energy sources is likely to be the usage of hydrogen, mainly for fuel cells powering vehicles, small energy generators and numerous portable devices. The potential climate change caused by excessive CO_2 emissions from fossil fuel utilization is the main driver for accelerated developments in renewable based energy generation and biomass energy technology is one of the most prospective among all renewable energy sources. Moreover, biomass can fractionally replace and coexist with the fossil fuels in the existing power generation technologies without the requirements for large and capital intensive engineering adjustments [1].

Biomass is an organic material from plants or animals, including forest product wastes, agricultural residues and waste, energy crops, animal manures and the organic component of municipal solid waste and industrial waste [2]. This organic

matter is processed to create bioenergy in form of electricity, heat, steam, and fuels. Consequently, bioenergy is defined as the energy produced from biomass. Organic matter either be used directly as a fuel processed into liquids and gases or be a residual of processing and conversion. Nowadays, biomass is considered as the major global primary energy sources and its modernized systems have been suggested to be critical to the future sustainable energy systems and to sustainable development in the developing countries. The utilization of bioenergy is increasing more and more during last years, and new technologies and researches are being developed in order to convert new sources of biomass into energy. Some of the advantages on bioenergy utilization are shown on the Table 1.1.

Table 1.1. Advantages and disadvantages on biomass utilization [3].

Advantages	**Disadvantages**
Renewable source of energy	Low density
High calorific value	High moisture content
Zero CO_2 effect	High transportation costs
Abundant	Reason for deforestation
Can be found as waste	High oxygen to carbon ratio
Cheap	Particulate emissions
Low sulphur and nitrogen content	Difficult to mill and crush
Low ash content	Seasonality
Low trace metal composition	Can contribute to global warming if harvested and utilized unsustainably
Oportunity for fast growing energy crops	

Advances in biotechnologies let anticipate the growing usage of biofuels. Different types of biofuels can be produced from biomass with physical operations such as grinding, drying, filtration, extraction and briquetting, and conversion processes such as biochemical and thermochemical processes. As biofuel biodiesel has proven itself as a technically sufficient alternative diesel fuel due to its alternative, non-toxic, biodegradable, and renewable nature in the fuel market since the beginning of

1980’s. It’s position gained in strength in the fuel market after the completion of its both EU and USA standards in 2002. Biodiesel is utilized as an alternative fuel in automobiles, heating systems and generators [1].

2. THEORETICAL PART

2.1. World, Spain and Turkey's fossil fuels energy profile

The global primary energy consumption increased by 2.4 % in 2007, when 2006 consumption values are considered [4]. Reserves, consumption and production values of world, Spain and Turkey's fossil fuel resources in 2007 are given in Table 2.1, 2.2 and 2.3 respectively. Moreover, world proved oil, natural gas and coal reserves have 45, 72 and 252 years of reserve life-time, respectively [5]. Oil has the biggest share in consumption in the world, Spain and Turkey, with 40.7%, 72.3% and 51.4%, respectively. Both countries Spain and Turkey have a high consumption in oil and natural gas in comparison to their production, for that big amounts of those fuels are imported every year. Coal consumption is not much higher than production and their reserves are large.

Table 2.1: World's reserves, consumption and production of fossil fuels in 2007 [4,6].

	Oil (M. Tonnes)	**Natural Gas (Mtoe)**	**Coal (Mtoe)**
Reserves	168600	157000	590700
Production	3906	2610	3122
Consumption	3953	2590	3164

Table 2.2: Spain's reserves, consumption and production of fossil fuels in 2007 [4,6].

	Oil (M. Tonnes)	**Natural Gas (Mtoe)**	**Coal (Mtoe)**
Reserves	20.40	2.22	407.05
Production	1.40	0.07	0.01
Consumption	80.50	30.58	0.03

Table 2.3: Turkey's reserves, consumption and production of fossil fuels in 2007 [4,6].

	Oil (M. Tonnes)	Natural Gas (Mtoe)	Coal (Mtoe)
Reserves	40.80	7.56	1394
Production	2.30	0.80	0.06
Consumption	34.50	32.53	0.07

2.2. World, Spain and Turkey renewable energy profile

2.2.1. World

In 2006, about 18% of global final energy consumption came from renewables, with 13% coming from traditional biomass, such as wood-burning. Hydroelectricity was the next largest renewable source, providing 3% (15% of global electricity generation), followed by solar thermal power, which contributed 1.3%. Modern technologies, such as geothermal energy, wind power, solar power, and ocean energy together provided some 0.8% of final energy consumption [7].

Wind power is growing at the rate of 30% annually, with a worldwide installed capacity of over 100 GW, and is widely used in several European countries and the United States. The manufacturing output of the photovoltaics industry reached more than 2000 MW in 2006, and photovoltaic power stations are particularly popular in Germany and Spain. Solar thermal power stations operate in the USA and Spain, and the largest of these is the 354 MW solar energy generation system power plant in the Mojave Desert, California. The world's largest geothermal power installation is The Geysers in California, with a rated capacity of 750 MW. Brazil has one of the largest renewable energy programs in the world, involving production of ethanol fuel from sugar cane, and ethanol now provides 18% of the country's automotive fuel. Ethanol fuel is also widely available in the USA, while in Europe the most produced biofuel is biodiesel [7].

2.2.2. Spain

Spain has the target of generating 30% of its electricity needs from renewable energy sources by 2010, with half of that amount coming from wind power. In 2006, 20% of the total electricity demand was already produced with renewable energy sources, being the hydropower and wind energies the largest ones with a contribution of 29301 and 22942 GWh, respectively. In January 2009 the total electricity demand produced with renewable energy sources reached 34.8% [8]. Table 2.4 provides the data of electricity production along with energy production and consumption from renewable energies in Spain in 2006.

According to wind power generation, Spain is the world's third biggest producer of this energy, after the United States and Germany, with an installed capacity of 16740 MW at the end of 2008, a rise of 1609 MW for the year. The largest producer of wind power in Spain is Iberdrola, with 27% of capacity, followed by Acciona on 16% and Endesa with 10%. Steady growth in capacity is expected in 2009, despite the credit crunch, due to long-term investments. Spain's wind farms are on track to meet a government target of 20000 MW in capacity by 2010 [9].

Spain is one of the most attractive countries for the development of solar energy, as it has more available sunshine than any other European country. In 2005 Spain became the first country in the world to require the installation of photovoltaic electricity generation in new buildings, and the second in the world, after Israel, to require the installation of solar hot water systems. The Spanish government is committed to achieving a target of 12% of primary energy from renewable energy by 2010 with an installed solar generating capacity of 3000 MW [10]. Spain is the fourth largest manufacturer in the world of solar power technology and in 2005 exported 80% of this output to Germany [11].

Table 2.4: Electricity production, energy production and consumption of renewable energy in Spain in 2006 [7].

	Electricity prod. (GWh)	Production (TJ)	Consumption (TJ)
Municipal waste	1921	14297	0
Industrial waste	0	0	0
Solid biomass	2167	181078	145709
Biogas	666	14002	1561
Liquid biofuels	0	242000	242000
Geothermal	0	322	322
Solar thermal	0	3067	3063
Hydropower	29301	-	-
Photovoltaics	97	-	-
Wave and ocean	0	-	-
Wind	22924	-	-

Table 2.5: Transformation of the energy production from renewable energies in Spain in 2006 [6].

	Electricity plants (TJ)	CHP plants (TJ)
Municipal waste	14297	0
Industrial waste	0	0
Solid biomass	22467	12744
Biogas	11880	560
Liquid biofuels	0	0
Geothermal	0	0
Solar thermal	2	0

Table 2.6: Specific consumption of the renewable energy in Spain in 2006 [6].

	Industry (TJ)	Transport (TJ)	Residential (TJ)	Commercial (TJ)	Agriculture (TJ)	Others (TJ)
Municipal waste	0	0	0	0	0	0
Industrial waste	0	0	0	0	0	0
Solid biomass	56925	0	85034	2688	766	296
Biogas	757	0	0	801	3	0
Liquid biofuels	0	242000	0	0	0	0
Geothermal	0	0	1	26	295	0
Solar thermal	63	0	2055	862	29	54

Some autonomous regions in Spain lead Europe in the use of renewable energy technology, and plan to reach 100% renewable energy generation in a few years. Castilla y León and Galicia are especially near this goal, producing in 2006 70% of their total electricity demand from renewable energy sources, and 5 communities produce more than 50% from renewables. Table 2.7 presents the energy production by region in Spain in 2006, and Figure 2.1 shows where are these regions located.

Figure 2.1: Map of Spain and its autonomous communities [13].

Table 2.7. Electricity from renewables in Spain by autonomous community in 2006. All the amounts are expressed in GWh [12].

Autonomous community	Hydroelectric power	Wind power	Solar power	Biomass power	Solid waste power	Total renewable generation	Total electricity demand	% Renewable of total electricity demand
Galicia	7561	5970	1	242	317	14091	20279	69.5%
Castilla y León	6960	3840	14	274	87	11175	15793	70.8%
Aragón	3073	3342	1	63	8	6487	11885	54.6%
Castilla La Mancha	710	3935	8	99	34	4786	12686	37.7%
Catalunya	3223	301	7	77	241	3849	48498	7.9%
Navarra	379	2248	28	269	0	2924	5401	54.1%
Andalucía	946	1042	5	728	0	2721	40737	6.7%
Asturias	1680	357	0	221	400	2658	12391	21.5%
Extremadura	2244	0	1	0	0	2245	5076	44.2%
Valencia	1041	266	13	55	0	1375	27668	5.0%
Euskadi	336	339	3	55	326	1059	20934	5.1%
La Rioja	124	897	1	3	2	1027	1860	55.2%
Cantabria	875	0	0	11	41	927	5693	16.3%
Madrid	83	0	8	58	330	479	30598	1.6%
Islas Canarias	0	288	0	0	0	288	9372	3.1%
Murcia	65	93	6	12	0	176	8334	2.1%
Illes Balears	0	5	0	0	133	138	6235	2.2%
Ceuta y Melilla	0	0	0	0	2	2	391	0.5%
SPAIN	29301	22924	97	2167	1921	5410	283829	19.9%

2.2.3. Turkey

The most signifiant renewable source to produce electricity in Turkey comes from the power of the water. Hydropower is by far the most important source and it contributed in 2006 with an amount of 44244 GWh, as shown in Table 2.8. Nowadays, Turkey counts on 22 dams and 19 hydroelectric stations built on the Euphrates and Tigris rivers in the 1980s and '90s in order to provide irrigation water and hydroelectricity to the arid southeastern Turkey, being the Atatürk Dam the largest one [15].

Turkey is located in an advantageous position in Europe for the purposes of solar power. Compared to the rest of Europe, insolation values are higher and conditions for solar power generation are comparable to Spain. The main solar energy utilization in Turkey is the flat plate collectors in the domestic hot water systems. The systems are mostly used in Aegean and Mediterranean regions.

Wind power in Turkey is gradually expanding in capacity. In 2006, 19 MW of wind power was installed, and in 2007, installed wind capacity increased to almost 140 MW [14]. Turkey is set to double the amount of its electricity supplied by wind power with the construction of a wind farm in southeast Turkey which will have an installed capacity of 135 MW when it is completed in 2009. The project will use 52 of the latest generation of turbines, each rated at 2.5 MW. Installed wind power is expected to reach 809 MW by the end of 2008. Wind energy potential for Turkey is 58 GW [14].

Turkey currently has the fifth highest direct usage and capacity of geothermal energy in the world. Turkey's capacity as of 2005 is 1495 MWt with a usage of 24840 TJ/year or 6900 GWh/year at a capacity factor of 0.53. Most of this is in the form of direct-use heating however geothermal electricity is currently produced at the Kizildere plant in the province of Denizli producing 120000 tons of liquid carbon dioxide and dry ice. The Kizildere plant has 20 MW capacity and runs at an average capacity of 12-15 MW annually [16].

Table 2.8: Electricity production, energy production and consumption of renewable energy in Turkey in 2006 [6].

	Electricity Production (GWh)	**Production (TJ)**	**Consumption (TJ)**
Municipal waste	0	0	0
Industrial waste	96	1152	0
Solid biomass	22	214924	214605
Biogas	35	331	0
Liquid biofuels	0	2000	2000
Geothermal	94	40974	37590
Solar thermal	0	16849	16849
Hydropower	44244	-	-
Photovoltaics	0	-	-
Wave and ocean	0	-	-
Wind	127	-	-

Table 2.9. Transformation of the energy production from renewable energies in Turkey in 2006 [6].

	Electricity plants (TJ)	**CHP plants (TJ)**
Municipal waste	0	0
Industrial waste	1152	0
Solid biomass	78	241
Biogas	295	36
Liquid biofuels	0	0
Geothermal	3384	0
Solar thermal	0	0

Table 2.10. Specific consumption of the renewable energy in Spain in 2006 [6].

	Industry (TJ)	Transport (TJ)	Residential (TJ)
Municipal waste	0	0	0
Industrial waste	0	0	0
Solid biomass	0	0	214605
Biogas	0	0	0
Liquid biofuels	0	2000	0
Geothermal	0	0	37590
Solar thermal	5086	0	11763

2.3. Biofuels

Biofuels are liquid fuels derived from organic matter or biomass [2]. Three generations of biofuels are currently existing. These generations have been appearing since today due to the researches on feedstocks, and they always are improving efficiency and economy of raw materials of biobuels.

The first-generation of biofuels covers biodiesel, bioethanol, ETBE and biogas. Feedstocks are harvested for their sugar, starch or oil content and can be converted into liquid fuels using conventional technology. The most well-known first-generation biofuel is ethanol made by fermenting sugar extracted from sugar cane or sugar beets, or sugar extracted from starch contained in maize kernels or other starch-laden crops. Similar processing, but with different fermentation organisms, can yield another alcohol, butanol. Commercialization efforts for butanol are ongoing, while ethanol is already a well-established industry. Biodiesel made from oil-seed crops is the other well-known first-generation biofuel [17]

Second-generation biofuels share the feature of being produced from lignocellulosic biomass, enabling the use of lower-cost, non-edible feedstocks, thereby limiting

direct food vs. fuel competition. This generation of biofuels can be classified in terms of the processes used to convert the biomass to fuel: biochemical or thermochemical. Second-generation ethanol or butanol would be made via biochemical processing. The fuels obtained from thermochemical processes include Fischer-Tropsch liquids (FTL), methanol, and dimethyl ether (DME). These fuels are made from sustainable sources that are not widely used: forest residues (e.g. sawdust), industry residues (e.g. black liquor from the paper industry), agricultural residues (e.g. corn stover), municipal waste and sustainable grown biomass (also listed under 3rd generation). Nowadays there are no technical production hurdles but market accessibility and economic benefits need to be addressed. [17]

The third-generation biofuels are made out of sustainable, non-food biomass sources such as algae, switch grass, jatropha, babassu and halophytes [18].

Algae are simple, photosynthetic plants that can be grown with polluted or salt water and can produce up to 250 times more oil than first-generation soybeans. Jatropha reclaims wasteland, is a natural fence for crops and grows in poor soils. Switchgrass, a hardy grass, needs little water and produces a high output of biomass [18].

These types of biofuels are starting to look very promising, but further research is required and volumes need to be expanded. [18]

2.3.1. Technology conversion for biofuels

The overall chain of biomass production, conversion to biofuels and end use is complex and requires integrated collaboration of many diverse stakeholder groups; farmers, foresters, engineers, chemical companies, fuel distributors, engine designers and vehicle manufacturers. In order to cover this complexity and understand the flow of activities that have to been processed, the process is divided into three steps: biomass production or feedstocks, conversion processes and product end-use. The figure 1 shows the main technology conversion from biomass to biofuels.

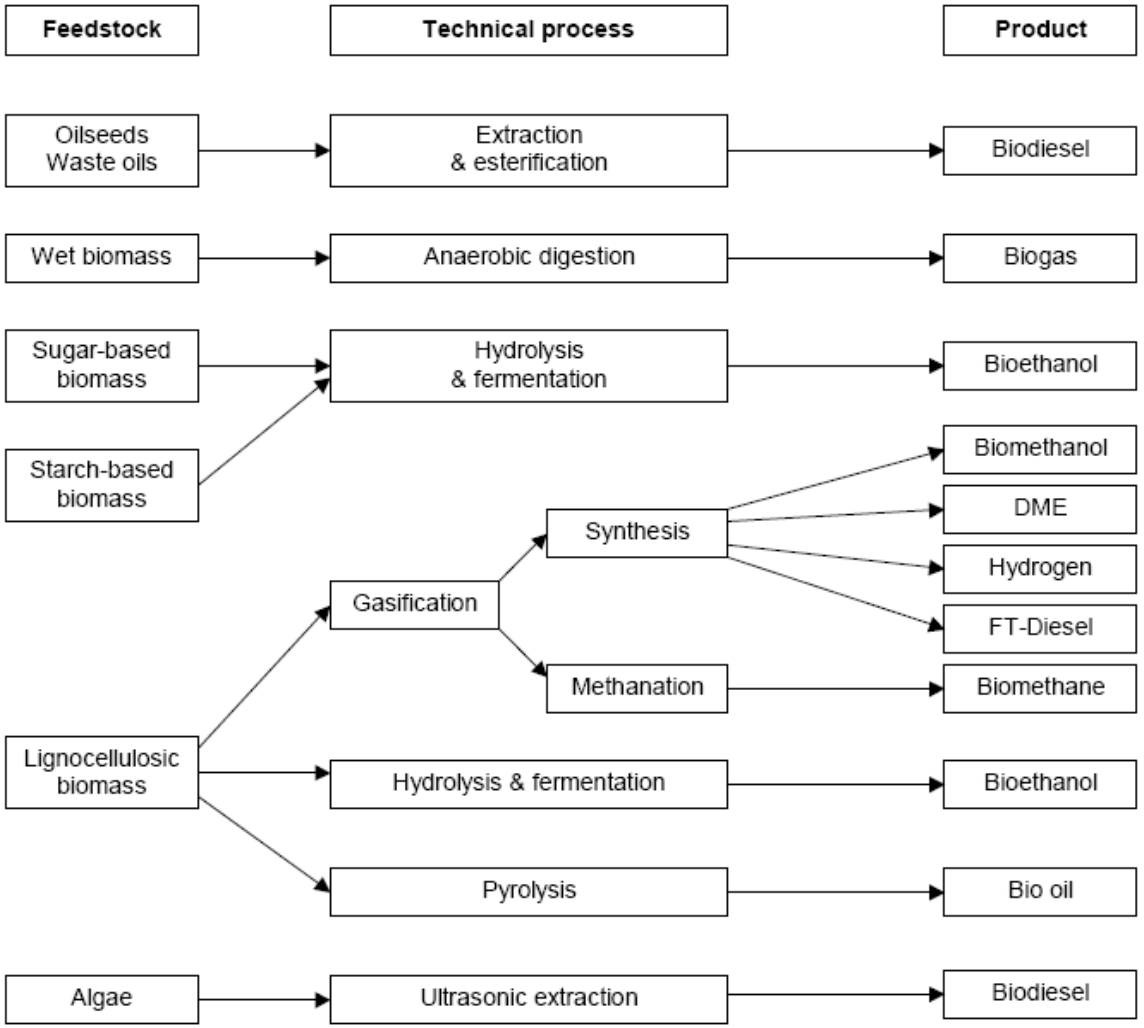

Figure 2.2. Biofuels conversion technologies [2, 17, 19].

2.3.2. Biofuels feedstocks

The material used as raw material in a industrial process is known as feedstock. [2] In the case of biofuels, those feedstocks come from biomass. On the table below there is shown the most important feedstocks organized by groups depending on their type of energy content.

Table 2.11: Classification of biofuels feedstocks [20].

Group	Feedstocks
Oilseed crops & waste oils	Corn, oats, cotton, soybean, mustard, camelina, crambe, rice, sunflower, peanut, rapeseed, coconut, oil palm, animal fats, waste oils.
Wet biomass	Agricultural or food processing by-products low in plant fibre and high in water content (70-90% water).
Sugar-based biomass	Sugar beets, sugar cane, sweet sorghum.
Starch-based biomass	Corn, barley, rye, wheat, sorghum grain, cassava, potatoes.
Lignocellulosic biomass	Willows, poplar, switchgrass, straw, corn stover, bagasse, forest redidues, paper waste, municipal solid waste.
Algae	Algae.

2.3.3. Final products

- Biodiesel

Biodiesel is a biofuel used in compression-ignition engines containing mono-alkyl esters of long chain fatty acids created by transesterifying plant or animal oils with a simple alcohol (methanol, ethanol) and a catalyst. Biofuels for diesel engines can also be produced from lignocellulosic biomass. The therm ‘biodiesel’ typically applies only to those fuels derived from renewable lipid sources [2].

- Bioethanol

Bioethanol is a vehicle fuel made from fermenting sugar derived from biomass that can replace ordinary gasoline in modest percentages (blends) in spark-ignition engines or can be used in pure form in specially modified vehicles [2].

- Biogas

Bio-gas typically refers to a gas produced by the biological breakdown of organic matter in the absence of oxygen. Biogas originates from biogenic material and is a type of biofuel. One type of bio-gas is produced by anaerobic digestion or fermentation of biodegradable materials such as biomass, manure or sewage, municipal waste, green waste and energy crops. This type of biogas comprises primarily methane and carbon dioxide. The other principal type of biogas is wood gas which is created by gasification of wood or other biomass. This type of biogas is comprised primarily of nitrogen, hydrogen, and carbon monoxide, with trace amounts of methane [2].

- Biomethanol

Biomethanol or methanol is an alcohol fuel derived from biomass and produced from synthesis gas. Methanol has been proposed as a fuel for internal combustion and other engines, mainly in combination with gasoline. Methanol fuel has received less attention than ethanol fuel as an alternative to petroleum based fuels [2].

- Biomethane

Methane (CH_4) is a colour- and odourless fuel and very well suited to be used in spark ignited internal combustion engines. The octane number of about 130 for pure methane is much higher then the one of gasoline. One important difference of bio-methane to other bio-fuels is that it can be produced very efficiently from almost any biogenic source (green waste, wood, liquid manure) and it does not compete with food production [21].

- Hydrogen

Eventually hydrogen will join electricity as the major energy carrier, supplying every end-use energy need in the economy, including transportation, central and distributed electric power, portable power, and combined heat and power for buildings and industrial processes. Fuel cells have the potential to replace the internal combustion engine in vehicles and to provide power in stationary and portable power applications because they are energy-efficient, clean, and fuel-flexible. But today, hydrogen fuel cell vehicles (FCVs) are currently in the pre-production stage of development, and the infrastructure to refuel them does not currently exist [31].

- Dimethyl ether

Dimethyl ether (DME) is the organic compound with the formula CH_3OCH_3. The simplest ether, it is a colourless gas that is a useful precursor to other organic compounds and an aerosol propellant. DME is also a promising clean-burning hydrocarbon fuel in diesel engines, petrol engines (30% DME / 70% LPG), and gas turbines, owing to its high cetane number, which is greater than 55 compared to diesel, which is 40–53. Only moderate modification are needed to convert a diesel engine to burn DME. The simplicity of this short carbon chain compound leads during combustion to very low emissions of particulate matter, NO_x, CO [19].

- Bio-oil

Bio-oil is an organic, liquid fuel produced through a process known as pyrolysis. Bio-oil is composed of hundreds of different chemicals, ranging from volatile compounds like formaldehyde and acetic acid to more stable phenols and anhydrous sugars. Its heating value compares with air-dried wood, methanol, and ethanol. The nearest term commercial use of bio-oil is in generation of power and heat. With modest equipment modifications, bio-oil can be substituted for fuel oil or diesel in a number of static applications including stationary diesel engines, gas turbines, boilers and furnaces. Bio-oil is derived from renewable resources, and is considered a renewable fuel [19].

2.3.4. Life cycle of biofuels

The ongoing climate change has its mayor origin in the combustion of fossils, like natural gas and oil. It is very important to note that the burning of biomass (bioenergy), like fossil fuels, can produce carbon dioxide. However, bioenergy creates what has been termed “net gain of zero”. This is because the small amount of emissions, mainly CO_2, put into the atmosphere by burning biomass is offset by the amount of CO_2 that was absorbed by the biomass when it was growing [3].

In the life cycle of biofuels, the relatively high production costs still remain a critical barrier to commercial development, although continuing improvements are achieved. Nevertheless, technologies for pure plant oil and biodiesel production from oilseed crops are already fairly mature.

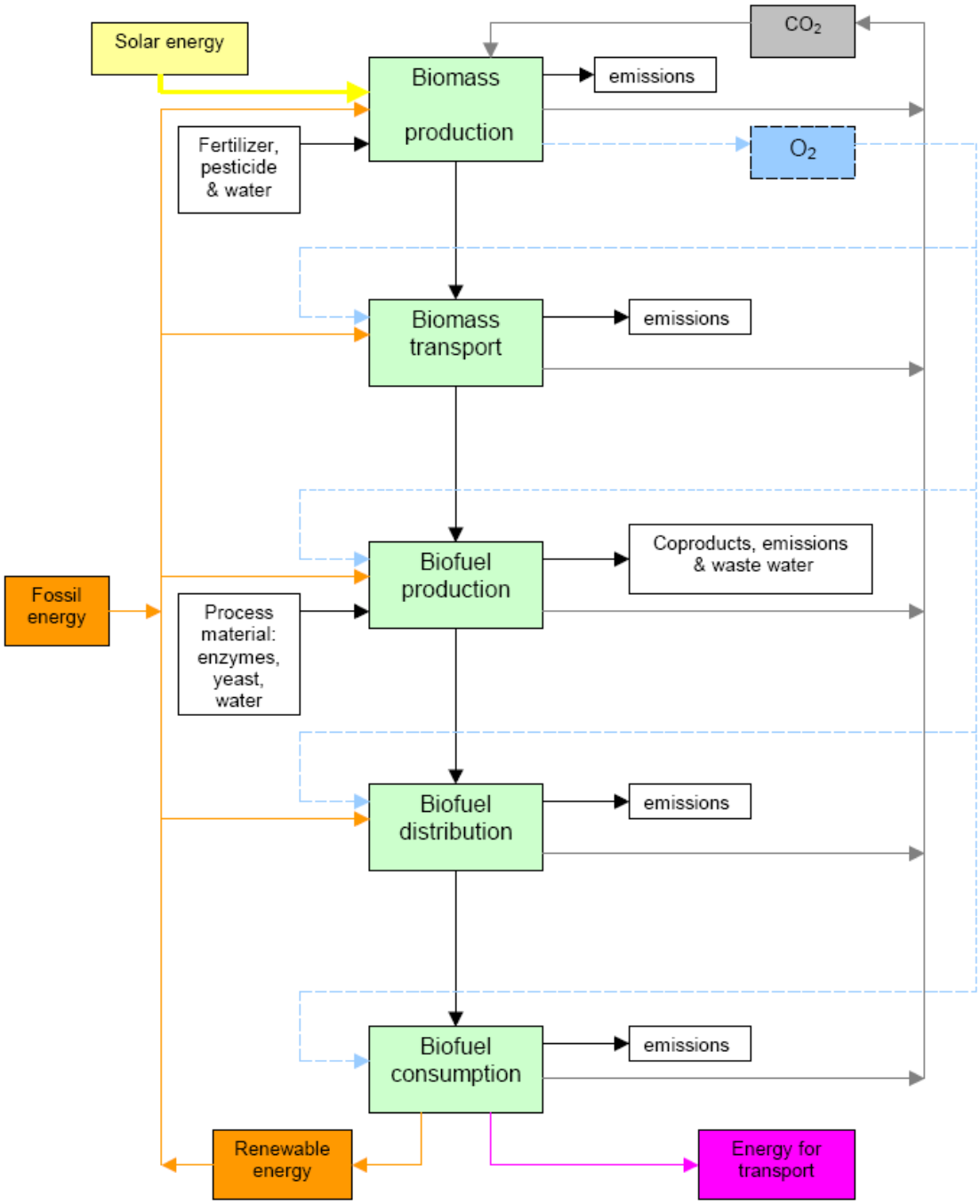

Figure 2.3. Energy flow and emissions in the life cycle of biofuels [20].

2.3.5. Biofuels policies

The competitiveness of biofuels will increase as the price for crude oil and other fossil sources increase, but today biofuel competitiveness still largely depends on the national legislative frameworks and subsidies in EU member states[1] .

The Spanish Congress approved a law on July 2008 in order to make the use of biofuels compulsory. At the beginning of 2009 a 3.4% of biofuels will be obligatory. The next year, 2010, this amount will increase to 5.75% of biofuel in blend due to the EU legislation. Finally, in 2020 EU has to blend at least a 10% in all of its biofuels [22].

Turkey does not have a legal framework to impulse the use of biofuels. Although some of the oil companies blend biofuels in the amount of 2%. While the biofuels output in Turkey is under no obligation to comply with the EU's 5.75% target, companies of biofuels are looking to reach that number [23].

If the adequate policy initiatives are provided, by 2025, 30% of the direct fuels use and 60% of global electricity supplies are expected to be met by renewable energy sources [3].

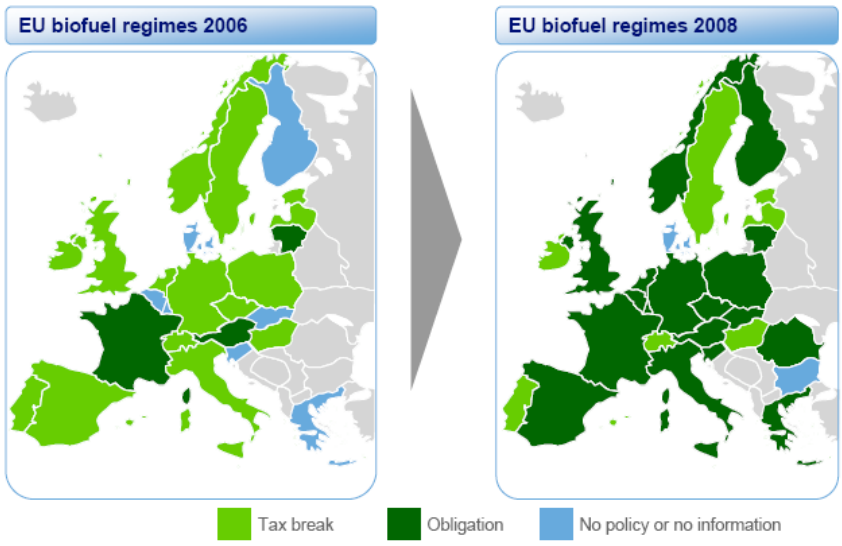

Figure 2.4. EU biofuel policies [22].

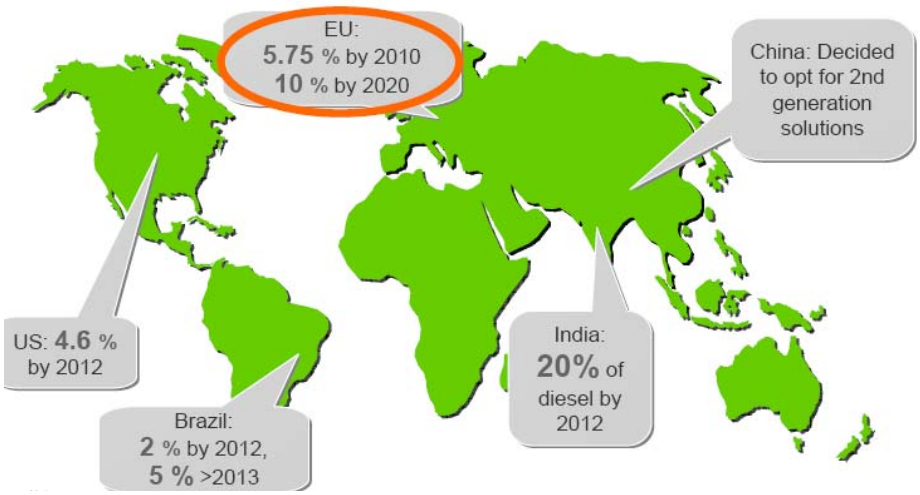

Figure 2.5. Future world targets in biofuels use [22].

Some of the future targets in the world are:

- EU target: 5.75% (energy content) biocomponent penetration in road fuels by 2010, 10% alternative fuels in road transport by 2020
- US target: 4.6% of 2012 gasoline demand to come from renewable fuel components.
- India target: 20% of diesel pool from biocomponents by 2012, 10% ethanol in gasoline by 2010.

2.4. Biodiesel

Biodiesel is a biofuel used in a compression-ignition engines containing mono-alkyl esters of long chain fatty acids created by transesterifying plant or animal oils with a simple alcohol (typically methanol, but sometimes ethanol) and a catalyst. Biofuel for diesel engines can also be produced from lignocellulosic biomass using gasification and synthesis, pyrolysis or hydrothermal liquefaction; however, the term 'biodiesel' applies only to those fuels derived from renewable lipid sources [2].

In 1900, Rudolf Diesel demonstrated his compression ignition engine at the World's Exhibition in Paris. In that prototype engine he used peanut oil, the first biodiesel. Vegetable oils were used until the 1920's when an alteration was made to the engine enabling it to use a residue of petroleum diesel. Although the diesel engine gained worldwide acceptance, biodiesel did not. With superior price, availability, and

government subsidies, petroleum diesel quickly became the fuel of choice for the diesel engine. In the mid 1970s, fuel shortages revived interest in developing biodiesel as an alternative to petroleum diesel. However, as the petroleum market was increasingly subsidized, biodiesel was again relegated to a minority alternative status. This political and economic struggle continues to limit the impact of the biodiesel industry today. Now, increasing concerns about the potential of global climate change, declining air and water quality, and serious human health concerns are inspiring the development of biodiesel, as a renewable, cleaner burning diesel alternative [20].

2.4.1. Feedstocks

Biodiesel can be made from many sources of oil and fats. Feedstocks of biodiesel can be classified into five groups according to their origin. We can see this classification on the table 2.12. Another classification for this feedstocks can be done according to the source of oil and it is shown on Table 2.13.

Table 2.12: Feedstocks for biodiesel [24].

Group	Source of oil
Major oils	Coconut, corn (maize), cottonseed, canola (a variety of rapeseed), olive, peanut, safflower, sesame, soybean, and sunflower
Nut oils	Almond, cashew, hazelnut, macadamia, pecan, pistachio and walnut
Other edible oils	Amaranth, apricot, argan, artichoke, avocado, babassu, bay laurel, beech nut, ben, Borneo tallow nut, carob pod, cohune, coriander seed, false flax, grape seed, hemp, kapok seed, lallemantia, lemon seed, macauba fruit, meadowfoam seed, mustard, okra seed (hibiscus seed), perilla seed, pequi,pine nut, poppy seed, prune kernel, quinoa, ramtil, rice bran, tallow, tea (camellia), thistle and wheat germ
Inedible oils	Algae, babassu tree, copaiba, honge, jatropha or ratanjyote, jojoba, karanja or honge, mahua, milk bush, nagchampa, neem, petroleum nut, rubber seed tree, silk cotton tree, and tall

Table 2.13. Oil content and main producer countries of the most used feedstocks for biodiesel. 1-Oilseed crops, 2-Palm fruit crops, 3-Algae, 4-Waste oil, 5-Lignocellulosic biomass [20, 25].

	Feedstock	**Oil Content (L/ Hectare)**	**Country**
1	Rapeseeds	1155	EU, China, India
	Soybeans	436	US, Brazil, Argentina
	Sunflowers	909	EU
	Jatropha	1836	India
	Cotton	318	India,US, Pakistan
	Peanut	1027	China, India, US
	Mustard	555	India, US
2	Palm oil	5773	Malaysia, Indonesia, Nigeria, EU
	Coconut	2.609	Philippines
3	Algae	110000	-
4	Frying oil	-	-
	Animal fat	-	-
5	Wood residues	-	-
	Municipal solid waste	-	-
	Crop residues	-	-
	Energy cops	-	-

Table 2.14. Oil and fat feedstock distribution of biodiesel in 2006 [25].

Feedstock	**%**
Animal fats	52
Soybean oil	20
Rapeseed oil	11
Palm oil	6
Sunflower oil	5
Other vegetable oils	5

The main feedstocks of biodiesel are described on the text below.

- Oilseed crops

Rapessed

Rapessed is the primary feedstock for biodiesel production in Europe. The continent's biodiesel producers typically have special arrangements with their governments to produce a certain amount of feedstock for biofuel production, usually on set-aside land. Rapeseed yields a lower quantity of fuel per hectare than starchy crops such as wheat and sugar beet. Commonly grown in rotation with cereal crops, it is a relatively productive oilseed and accounts for the highest output of biodiesel per hectare in the EU in comparison to soybeans and sunflower seed [2].

Soybeans

Soybeans are the dominant oilseed crop cultivated worldwide, far surpassing the output of the other oil crops. Brazil, the US and Argentina dominate world soybean production, accounting for an estimated 30 per cent of the global supply for export. Although soybeans generate a relatively low yield of biodiesel per hectare when

compared to other oilseed crops, they can grow in both temperate and tropical conditions. As a nitrogen-fixing crop, they also replenish soil nitrogen and require less fertilizer input, giving them a relatively favourable fossil energy balance. Soybeans are growing in rotation with corn in US, and with sugar in Brazil. Only a small fraction of the soybean supply is currently transformed into fuels [2].

Jatropha

Jatropha curcas is an oilseed crop that grows well on marginal and semi-arid lands. The blushes can be harvested twice annually, are rarely browsed by livestock and remain productive for decades. Jatropha has been identified as one of the most promising feedstocks for large-scale biodiesel production in India, where nearly 64 million hectares of land is classified as wasteland or uncultivated land. It is also particularly well suited for fuel use at the small-scale or village level [2].

- Palm fruit crops

Palm is an attractive candidate for biodiesel production because it yields a very high level of oil per hectare. The two largest producers are Malaysia and Indonesia, where palm oil production has grown rapidly over the last decade. While most palm oil is used for food purposes, the demand for palm biodiesel is expected to increase in a short time, particularly in Europe [2].

- Algae

Algae oil is an interesting sustainable feedstock for biodiesel manufacturing. It is an alternative to popular feedstocks, like soybean, canola and palm. Ultrasonication improves the extraction of oil from the algae cells and the conversion to biodiesel [26].

Algae can grow practically anywhere where there is enough sunshine. Some algae can grow in saline water. All algae contain proteins, carbohydrates, lipids and nucleic acids in varying proportions. While the percentages vary with the type of algae, there are algae types that are comprised up to 40% of their overall mass by fatty acids. The most significant distinguishing characteristic of algal oil is its yield and hence its biodiesel yield. According to some estimates, the yield (per hectare) of oil from algae is over 200 times the yield from the best-performing plant/vegetable

oil. Microalgae are the fastest-growing photosynthesizing organisms. They can complete an entire growing cycle every few days. Approximately 46 tons of oil/hectare/year can be produced from diatom algae. Different algae species produce different amounts of oil. Some algae produce up to 50% oil by weight. The production of algae to harvest oil for biodiesel has not been undertaken on a commercial scale, but working feasibility studies have been conducted to arrive at the above number [24].

Like other plants, algae stores energy in the form of lipids. There are various methods for extracting the oils, such as pressing, hexane solvent wash and ultrasonic extraction [26].

- Waste oils

Animal fats are co-products of meat and fishery industries. It can be received from cattle, hog, chicken and fish. Due to the low retail prices of these co-products they may be an increasing source for biodiesel production, especially in order to replace fuel for vehicle fleets of companies producing these raw materials [20].

Meat and bone meal is not allowed to be used as fodder any more and it is tested for its applicability to biofuel production. Tallow derived from infected cattle is also considered as an interesting feedstock. All these animal fats are characterized by high amounts of saturated fatty acids resulting in methyl esters poor cold temperature properties. The high degree of saturation makes animal fat methyl esters excellent fuels regarding heating value and cetane number. But these sources have some problems as the discontinuity of supply and the ethical aspect of using animal parts for transport fuel [20].

A large variety of waste fried oil is available for biodiesel production. In general these waste oils are inexpensive and offer an additional environmental impact by using substances which would otherwise have to be disposed. These oils can come from households, restaurants and food industry [20].

Table 2.15. Comparison of waste oil, biodiesel from waste oil and petrodiesel properties [24].

Fuel property	Waste coocking oil	Biodiesel from waste cooking oil	Petrodiesel
Density (kg/L, at 288 K)	0.924	0.897	0.075–0.840
Flash point (K)	485	469	340–358
Pour point (K)	284	262	254–260
Cetane number	49	54	40–46
Ash content (%)	0.006	0.004	0.008–0.010
Sulfur content (%)	0.09	0.06	0.35–0.55
Carbon residue (%)	0.46	0.33	0.35–0.40
Water content (%)	0.42	0.04	0.02–0.05
Higher heating value (MJ/kg)	41.40	42.65	45.62–46.48
Free fatty acid (mg KOH/g oil)	1.32	0.10	–
Saponification value	188.2	–	–
Iodine value	141.5	–	–

- Lignocellulosic biomass

Lignocellulosic biomass refers to biomass feedstock such as woody materials, grasses and agricultural and forestry residues, that contains cellulose, hemicellulose and lignin. It can be broken in a number of ways to be used as biofuels. The feedstocks can be classified in four groups: wood residues, municipal solid waste, crop residues, energy crops [2].

Wood residues

Forest fires has often led to an excess amount of undergrowth in forests that creates imbalances in the health of a forest. Creating a market for this woody undergrowth for use in biomas-to-liquid fuel applications may complement efforts to create healthier forests. Wood from pest or storm-damaged forests could also be a potential source of biomass for biofuel applications.

Much of the wood residues produced by the lumber industry are used to provide the energy needed for the lumber production process (such as lumber drying and cogeneration of heat and power), though some of this wood may be available for biofuels use [2].

Municipal solid waste

A mix of cellulosic material is typically present in municipal solid waste, including wood, paper, cardboard and waste fabrics. Since fees are charged to dispose of this waste, it could provide a supply of low or negative cost biomass for some early pioneer cellulose-to-biofuels facilities in urban areas [2].

Crop residues

Crop residues in the form of stems and leaves from conventional food crop harvests represent a substantial quantity of cellulosic biomass produced each year. In many instances, much of this residue needs to be left in the field to provide protection from erosion and to provide benefits such as micronutrients supplies and soil organic matter. Removing any residue on some soils could reduce their quality, promote erosion and lead to a loss of soil carbon, which, in turn, lowers crop productivity and profitability. However, in cases where land is relatively flat and where conservation tillage methods are employed, a portion of the crop residues may be sustainably

harvested. Some level of removal can be beneficial [2].

Corn crops typically produce the largest amounts of crop residues per hectare of all of the main conventional crop types (these residues, known as stover, include the stalks, leaves and cobs of the plant after the grain is harvested. With either stover or straw, more could be harvested if no-till cultivation methods are adopted. Because they release less soil carbon, such techniques allow a grater portion of the crop residue to be harvested for biofuel use since less stover or straw would be needed to protect the soil from erosion and carbon losses [2].

In Brazil, more than 80% of the sugar cane harvest is manually. Before this cutting occurs, the tops and leaves of the cane are burned off to make harvesting safer and more productive for workers. However, plans are advancing to mechanize the cane harvest to avoid burning of fields, a practice that causes considerably air pollution. As technologies for converting cellulose to biofuels are commercialized, this should create markets for the cellulosic field residues from sugar cane harvesting [2].

Energy crops

Large amounts of cellulosic biomass could be produced via dedicated plantations of energy crops based on the use of perennial herbaceous plant species, or with the use of short-rotation woody crops. There are a number of reasons why energy crop production could be quite attractive, beyond offering the potential to substantially expand the supply of biomass feedstock. The plantation of energy crops progressively increases the soil's organic matter content. The roots of the perennial crops provide protection from erosion, and the crops generally require less intensive use of the fertilizers and pesticides, as well as less overall energy consumption for crop management [2].

2.4.2. Biodiesel production

There are many processes to obtain biodiesel because of the variety of raw materials that we have just seen on Table 2.12. For example, to obtain biodiesel from algae plants the most suitable technology conversion is ultrasonic extraction, but if biodiesel is made from lignocellulosic biomass a gasification and a Fischer-Tropsch synthesis will be needed.

- Ultrasonic extraction

Intense sonication of liquids generates sound waves that propagate into the liquid media resulting in alternating high-pressure and low-pressure cycles. During the low-pressure cycle, high-intensity small vacuum bubbles are created in the liquid. When the bubbles attain a certain size, they collapse violently during a high-pressure cycle. This is called cavitation. During the implosion very high pressures and high speed liquid jets are produced locally. The resulting shear forces break the cell structure mechanically and improve material transfer. This effect supports the extraction of lipids from algae [26].

- Fischer-Tropsch synthesis

The Fischer-Tropsch process is one of the advanced biofuel conversion technologies that comprise gasification of biomass feedstocks, cleaning and conditioning of the produced synthesis gas, and subsequent synthesis to liquid or gaseous biofuels. The Fischer-Tropsch process has been known since the 1920s in Germany, but in the past it was mainly used for the production of liquid fuels from coal or natural gas. However, the process using biomass as feedstock is still under development. Any type of biomass can be used as a feedstock, including woody and grassy materials and agricultural and forestry residues. The biomass is gasified to produce synthesis gas, which is a mixture of carbon monoxide and hydrogen. Prior to synthesis, this gas can be conditioned using the water gas shift to achieve the required H_2/CO ratio for the synthesis. The liquids produced from the syngas are very clean (sulphur free) straight-chain hydrocarbons, and can be converted further to automotive fuels [28].

- Gasification

Biomass gasification means incomplete combustion of biomass resulting in production of combustible gases consisting of carbon monoxide, hydrogen and traces of methane. This mixture is called producer gas. Producer gas can be used to run internal combustion engines (both compression and spark ignition), as substitute for furnace oil in direct heat applications and to produce, in an economically viable way, methanol. Since any biomass material can undergo gasification, this process is much more attractive than ethanol production or biogas where only selected biomass materials can produce the fuel [3, 29].

- Transesterification process

The amount of fuel production from algae, waste oils and lignocellulosic biomass is still small, although the potential is expected to be very high. The most used technology to convert oilseed and palm fruit crops into biodiesel is the transesterification process [20].

The first step of this process is the oil extraction. Regarding the scale of production and the infrastructure, there are two fundamental production process types for vegetable oils: industrial and small scale pressing. The process of oil extraction for the most of oilseed crops is similar to that of rape seed. Because of that, the example of the rape seed is given to explain the process. The common way in oil extraction is the treatment of feedstock in centralized industrial large scale plants. First, the feedstock has to be pre-treated. Within the pre-treatment the rape seeds have to be dried first, but only if it will be stored more than ten days. In this case, the typical water content of rape seeds, which is about 15%, has to be reduced to 9%. After that, the rape seeds are cleaned. It has to bear in mind that seeds that are large in size, such as sunflower seeds, have to be peeled. After this treatment seeds are crushed and temperature and moisture content are conditioned. Those conditions are important because too high or too low moisture content would make difficult the solvent penetration, as the oil flew is better as it is more liquid. And also an 80ºC temperature process is needed because it deactivates microorganisms, avoids smearing of the press through coagulate proteins and also makes a better penetration of the solvent. After conditioning, the oilseeds are pressed at the same temperature as before (80ºC). Thereby approximately 75% of the total rape oil content can be extracted. This pressed raw oil then is filtered and dehydrated and the final pure oil can be used for further refining for biodiesel production. The pressed rape seeds are left as co-product, because they still contain the remaining 25% of the total oil content and therefore are further treated. First, they have to be crushed so that the added solvent, which is usually hexane, can extract the oil at temperatures of up to 80ºC. The result of this process step are a mixture of oil with hexane, also called miscella, and the rest of the seed with hexane that is known as extraction grist. The solvent is separated from both compounds and recycled to the process [20].

The second part in this process is the refining. The refining consist of preparing the vegetable oil for the transesterification process of biodiesel. It is very important because undesirable substances such as phosphatides, free fatty acids, waxes, colourants and tocopherols are removed. This substances can alter oil storage life and hamper further processing. The process of refining has five steps, in order: degumming, deadification, bleaching, deodorization and dehydration. In the degumming the phosphatides are removed and it can happen by two different ways: addition of water at 60-90ºC with the obtention of two phases (oil and water with solvent) by centrifugal separation or addition of acid, generally citric or phosphoric. The first one is generally used for soluble phosphatides, and the second one for those which cannot be hydrated. The second refining step is the deacidification. In this process many substances, that can alter storage life and influence transestrification such as rancid flavours of free fatty acids, phenol, oxidized fatty compounds, heavy metals ans phosphatides, are removed. Several methods of deacidification are in operation: neutralization with alkali, distillation, deacidification by gentrification and deacidification and extraction of colourants and odours with solvents. In the bleaching step colourants are removed. It is important because it enhances storage life of the biofuel. Bleaching is mainly conducted by adsorbing substances, such as bleaching earth, silica gel or activate carbon. But also oxygen, ozone, hydrogen peroxide and heat (200ºC) can be used for bleaching. The fourth step, deodorization, consist of removing odorous substances by steam distillation. Finally a dehydration step has to be conducted, as traces of water may decrease conversion in the transesterification process of biodiesel production. The removal of water is either accomplished by distillation under pressure or by passing a steam of nitrogen though the fatty material [20].

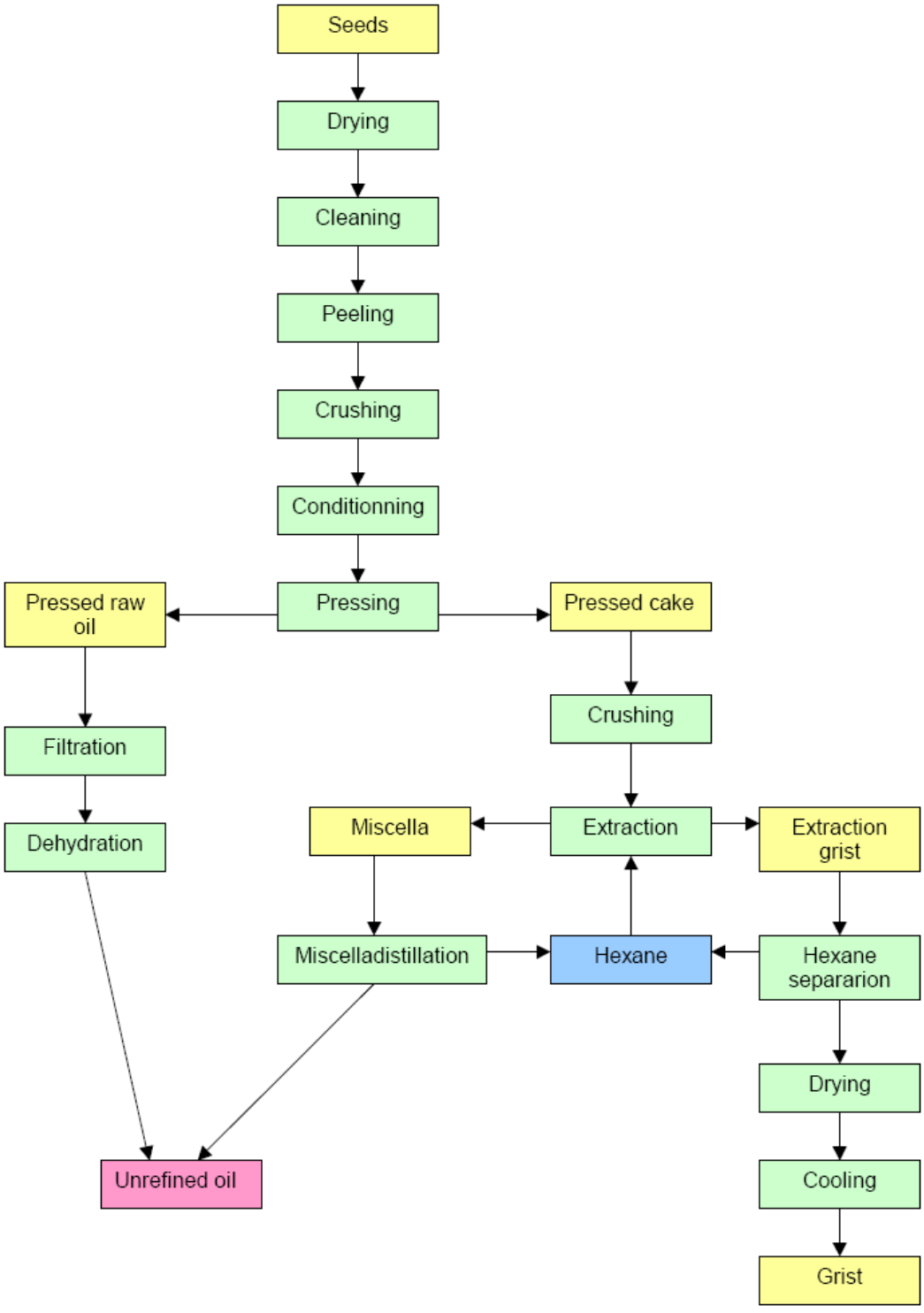

Figure 2.6. Oil extraction process of biodiesel [20].

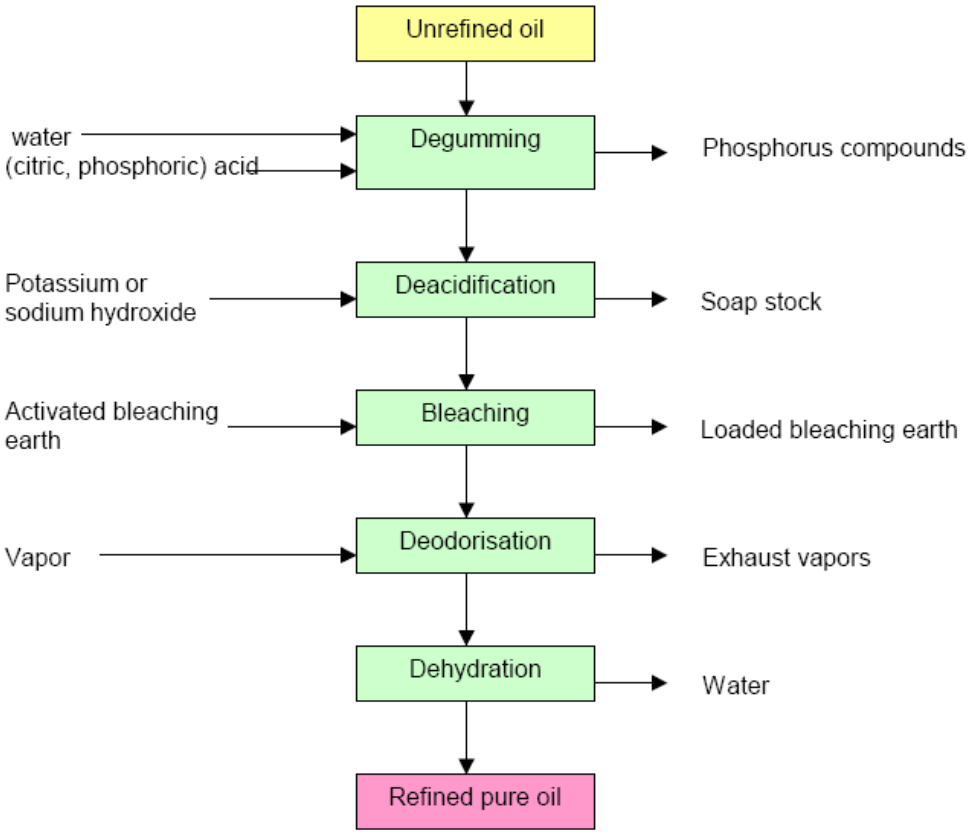

Figure 2.7. Oil refining process of biodiesel [20].

The chemical transesterification process during biodiesel production changes the molecular structure of lipid molecules. Thereby the physical properties change. Biodiesel is very similar to fossil diesel and thus can be consumed in common diesel engines which are refitted with only small efforts [20].

Transesterification, also called alcoholysis, is the process by which the refined oil molecule is cracked and the glycerine is removed, resulting in glycerine soap and methyl or ethyl esters (biodiesel). Organic fats and oils are triglycerides which are three hydrocarbon chains connected by glycerol. The bonds are broken by hydrolyzing them to form free fatty acids. These fatty acids are then mixed or reacted with methanol or ethanol forming methyl or ethyl fatty acid esters (monocarbon acid esters). The mixture separates and settles out leaving the glycerine on the bottom and the biodiesel (methyl-, ethyl ester) on the top. Now the separation of these two

substances has to be conducted completely and quickly to avoid a reversed reaction. Thee transesterification reactions are often catalysed by the addition of an acid or base. For the transesterification process, mainly the alcohols methanol and ethanol are used. Theoretically transesterification can be also processed with higher or secondary alcohols. Methanolysis (transesterification with methanol) is the most commonly method for biodiesel production due to its lower prices and its higher reactivity. This reaction can happen by heating a mixture of 80-90 percent oil, 10-20 percent methanol and small amounts of catalyst. The biodiesel after methanolysis is called fatty acid methyl ester (FAME). Ethanolysis (transesterification with ethanol) is more environmentally friendly, less toxic, increases heat contents and cetane number of the biofuel, but the disadvantages are that more energy is needed, problems with the separation of the ester and glycerin phases are reported more frequently and prices are higher than methanolysis. The biodiesel after ethanolysis is known as fatty acid ethyl ester (FAEE) [20].

Although the transesterification proceeds in the absence of catalyst as well, the reaction usually is conducted by using catalyst due to economic reasons. Non-catalytic reacting too slowly and high energy inputs are required. Several types of catalysts can be used such as alkaline material, acid material, transition metal compounds and silicates [20].

Table 2.16. Comparison of various methanolic transesterification methods [24].

Method	**Reaction temperature (K)**	**Reaction time (min)**
Acid or alkali catalytic process	303–338	60–360
Boron trifluoride–methanol	360–390	20–50
Sodium methoxide–catalyzed	293–298	4–6
Non-catalytic supercritical methanol	523–573	6–12
Catalytic supercritical methanol	523–573	0.5–1.5

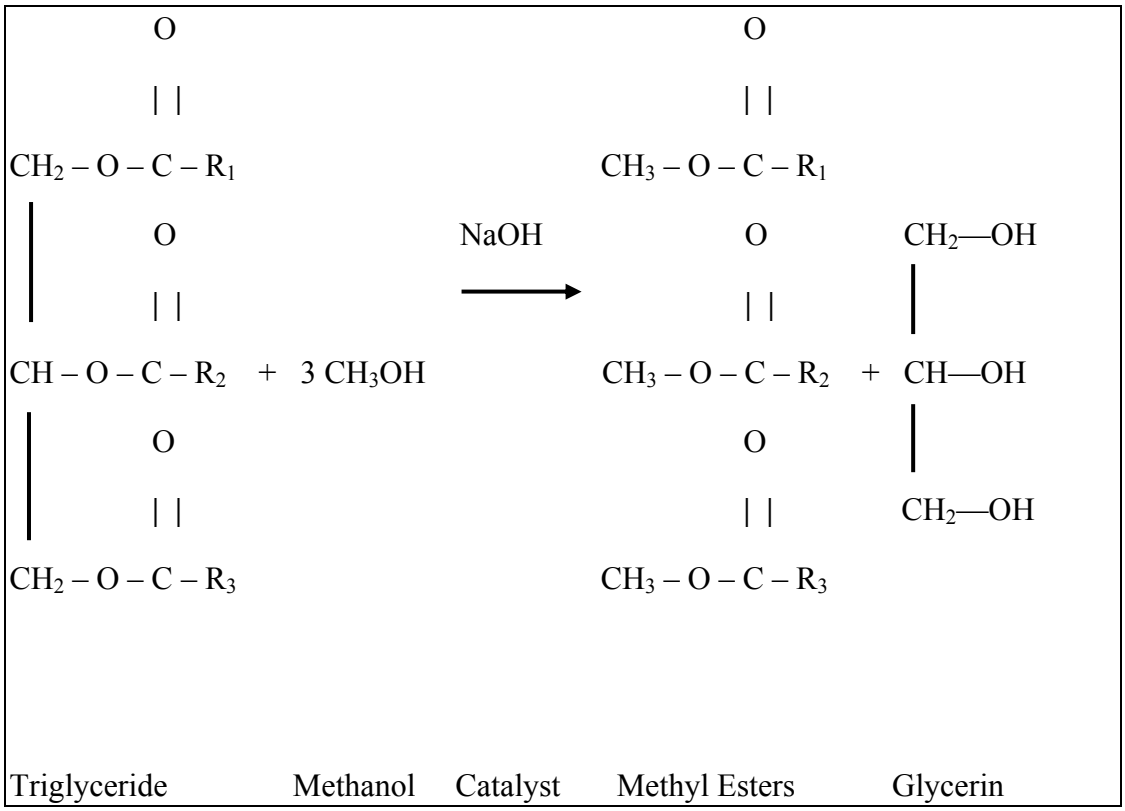

Figure 2.8. Reaction of transesterification of biodiesel [20].

2.4.3. Properties of biodiesel

Cetane number

The cetane number (CN) is one of the most commonly cited indicators of diesel fuel quality. It measures the readiness of the fuel to autoignite when injected into the engine. It is generally dependent on the composition of the fuel and can impact the engine's start ability, noise level, and exhaust emissions [30].

This number is based on two compounds, hexadecane, with a CN of 100, and heptamethylnonane, with a CN of 15. The CN is a measure of the ignition quality of diesel fuels, and a high CN implies short ignition delay. The CN of biodiesel is generally higher than conventional diesel. The longer the fatty acid carbon chains and the more saturated the molecules, the higher the CN. The CN of biodiesel from animal fats is higher than those of vegetable oils [24].

This property of biodiesel is generally observed to be quite high and values varying between 45 and 67. This number depends on the distribution of fatty acids in the original oil or fat from which it was produced. Fuel which has been distilled oxidizes

much more quickly than undistilled fuel. While the distillation process does not affect the cetane number, the oxidation results in a cetane number increase [30].

Biodiesel, from various feedstocks, tend to have higher cetane numbers than diesel so would therefore tend to improve operation of the engine when compared to diesel based on this parameter alone [30].

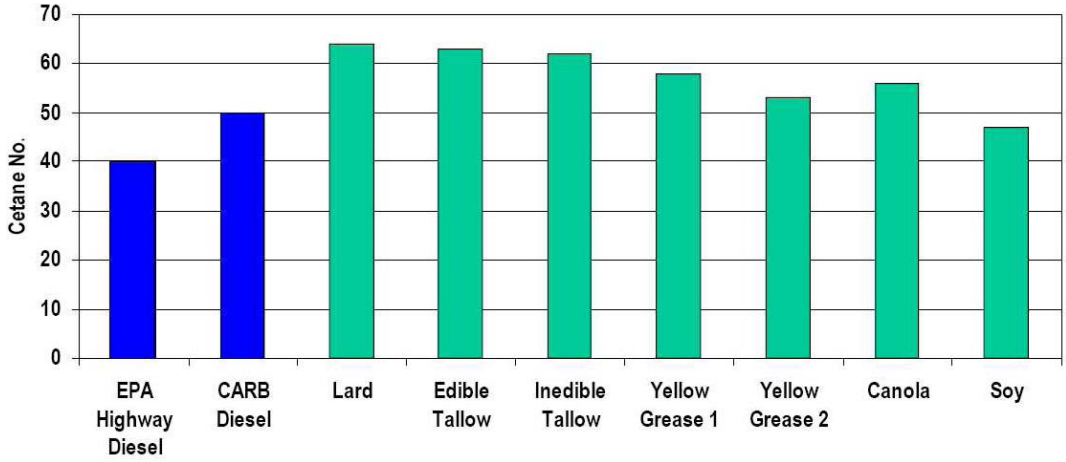

Figure 2.9: Comparison of cetane numbers in diferent feedstocks of biodiesel [31].

Emissions Reductions

The use of biodiesel in a conventional diesel engine results in substantial reduction of unburned hydrocarbons, carbon monoxide, and particulate matter. Emissions of nitrogen oxides are either slightly reduced or slightly increased depending on the duty cycle of the engine and testing methods employed. Particulate emissions from conventional diesel engines are generally divided into three components. Each component is present in varying degrees depending on fuel properties, engine design and operating parameters [30].

The first component, and the one most closely related to the visible smoke often associated with diesel exhaust, is the carbonanceous material. This material is composed of sub-micron sized carbon particles which are formed during the diesel combustion process. Is especially prevalent under conditions when the fuel-air ratio is overly rich [30].

The second component is hydrocarbon material which is absorbed on the carbon particles, commonly referred to as the soluble fraction. A portion of this material

results from incomplete combustion of the fuel. The remainder is derived from engine lube oil that passes by the piston oil rings [30].

The third particulate component is comprised of sulphates and bound water. The amount of this material is directly related to the fuel sulphur content [30].

The use of biodiesel decreases the solid carbon fraction of particulate matter (since the oxygen in biodiesel enables more complete combustion to CO_2), eliminates the sulphate fraction (as there is no sulphur in the fuel), while the soluble, or hydrocarbon, fraction stays the same or is increased and the NO_X emissions are higher [30].

Table 2.17. Emissions reduction for biodiesel blends B20 and B100 [31].

Emission Type	**B100**	**B20**
Unburned hydrocarbons	-67%	-20%
Carbon monoxide	-48%	-12%
Particulate matter	-47%	-12%
Sulfates	-100%	-20%
NO_X	+10%	+2%

Biodegradability

Biodiesel has desirable degradation attributes which make it the fuel of choice by environmentally conscious users. Biodiesel samples degrade more rapidly than dextrose, and are 95% degraded at the end of 28 days. The diesel fuel is approximately 40% degraded after 28 days.

It should also be noted that blending biodiesel with diesel fuel accelerates its biodegradability. For example blends of 20% biodiesel and 80% diesel fuel (B20) degrade twice as fast as current diesel and neat biodiesel degrades as fast as sugar. Thus, biodiesel use has demonstrated biodegradability benefits at levels lower than 100% [30].

Table 2.18. Biodegradability data of petroleum and biofuels [24].

Fuel sample	Degradation in 28 d (%)
Gasoline (91 octane)	28
Heavy fuel (Bunker C oil)	11
Refined rapeseed oil	78
Refined soybean oil	76
Rapeseed oil methyl ester	88
Sunflower seed oil methyl ester	90

Flash Point

The flash point of a fuel is defined as the temperature at which the fuel becomes a mixture that will ignite when exposed to a spark or flame. The flash point of biodiesel has been tested and reported by various sources. The flash point of biodiesel blends increases as the percentage of biodiesel increases. Therefore pure biodiesel and blends of biodiesel with petroleum diesel are safer to store, handle, and use than conventional diesel fuel. Neat biodiesel has a flash point over 410 K, well above the flash point of petroleum based diesel fuel [30].

Lubricity

Lubricity refers to the property of a lubricant that causes a difference in friction under conditions of boundary lubrication when all the known factors except the lubricant itself are the same. The lower the friction the higher the lubricity [32].

All diesel fuel injection equipment has some reliance on diesel fuel as a lubricant. The lubricating properties of diesel fuel are important, especially for rotary and distributor type fuel injection pumps. In these pumps, moving parts are lubricated by the fuel itself as it moves through the pump—not by the engine oil. Other diesel fuel systems—which include unit injectors, injectors, unit pumps, and in-line pumps are

partially fuel lubricated. In these systems the mechanism typically consists of a plunger or needle operating in a sleeve or bore, where the fuel is used to lubricate the walls between the reciprocating piece and its container. The lubricity of the fuel is an indication of the amount of wear or scarring that occurs between two metal parts covered with the fuel as they come in contact with each other. Low lubricity fuel may cause high wear and scarring and high lubricity fuel may provide reduced wear and longer component life [30].

The lubricity of diesel fuel can vary dramatically. It is dependent on a wide variety of factors, which include the crude oil source from which the fuel was produced, the refining processes used to produce the fuel, how the fuel has been handled throughout the distribution chain, and the inclusion of lubricity enhancing additives whether alone or in a package with other performance enhancing additives [30].

Biodiesel methyl esters improve the lubrication properties of the diesel fuel blend. Fuel injectors and some types of fuel pumps rely on fuel for lubrication. Biodiesel reduced long term engine wear in test diesel engines to less than half of what was observed in engines running on current low sulphur diesel fuel. Lubricity properties of fuel are important for reducing friction wear in engine components normally lubricated by the fuel. Biodiesel provides significant lubricity improvement over petroleum diesel fuel. Lubricity results of biodiesel and petroleum diesel using industry test methods indicate that there is a marked improvement in lubricity when biodiesel is added to conventional diesel fuel. Even biodiesel levels below 1% can provide up to a 30% increase in lubricity [24].

Stability

A fuel is considered unstable when it undergoes chemical changes that produce undesirable consequences such as deposits, acidity, or a bad smell. There are three different types of stability: thermal, oxidative, and storage stability.

Thermal stability addresses fuel changes that occur due to elevated temperature. These changes may occur at conditions commonly found in diesel fuel injection systems (60 - 100 ºC) and particularly at conditions found at the fuel injector tip (300 ºC).

Oxidative stability refers to the tendency of fuels to react with oxygen at temperatures near ambient. These reactions are much slower than those that would occur at combustion temperatures, and they produce varnish deposits and sediments. Storage stability is also a frequently used term and refers to the stability of the fuel while it is in long-term storage. These terms are not necessarily exclusive terms. For example, oxidative attack is probably one of the primary concerns of storage stability but storage stability might also involve issues of water contamination and microbial growth [30].

Vegetable oils are generally more susceptible to oxidative attack because they are less saturated, that is, they contain more carbon-carbon double bonds. When unsaturated oils, and the biodiesel made from them, are exposed to oxygen, the oxygen attaches to a carbon that is immediately adjacent to those involved in the double bond (a beta carbon). This forms a hydroperoxide molecule. The presence of these compounds is measured with the Peroxide Value, which is an indicator of early steps in the oxidation process [30].

Depending on the physical conditions for the oil, the hydroperoxides can either break apart to form short chain aldehydes and acids or they can attach together to form dimers and polymers. The short chain acids can be volatile and cause a foul smell, and a lowering of the flashpoint. Polymerization can cause an increase in viscosity and the formation of insoluble sediments and varnish deposits [30].

Cold flow

Two important parameters for low-temperature applications of a fuel are cloud point (CP) and pour point (PP). The CP is the temperature at which wax first becomes visible when the fuel is cooled. The PP is the temperature at which the amount of wax from a solution is sufficient to gel the fuel; thus it is the lowest temperature at which the fuel can flow. Biodiesel has a higher CP and PP compared to conventional diesel [24].

Calorific Value

The oxygen content of biodiesel improves the combustion process and decreases its oxidation potential. The structural oxygen content of a fuel improves its combustion efficiency due to an increase in the homogeneity of oxygen with the fuel during combustion. Because of this the combustion efficiency of biodiesel is higher than

that of petrodiesel, and the combustion efficiency of methanol/ethanol is higher than that of gasoline. A visual inspection of the injector types would indicate no difference between biodiesel fuels and petrodiesel in testing. The overall injector coking is considerably low. Biodiesel contains 11% oxygen by weight and no sulphur. The use of biodiesel can extend the life of diesel engines because it is more lubricating than petroleum diesel fuel. Biodiesel has better lubricant properties than petrodiesel. The higher heating values of biodiesels are relatively high. For biodiesels (39–41 MJ/kg) it is slightly lower than that of gasoline (46 MJ/kg), petrodiesel (43 MJ/kg), or petroleum (42 MJ/kg), but higher than coal (32–37 MJ/kg) [24].

Water content

The soap can prevent the separation of biodiesel from glycerol fraction. In catalysed methods, the presence of water has negative effects on the yields of methyl esters. On the other hand, water content of biodiesel reduces the heat of combustion. This means more smoke, harder starting, less power. Water will cause corrosion of vital fuel system components fuel pumps, injector pumps, fuel tubes, etc. Water, as it approaches 273 K begins to form ice crystals. These crystals provide sites of nucleation and accelerate the gelling of the residual fuel. Water is part of the respiration system of most microbes. Biodiesel is a great food for microbes and water is necessary for microbe respiration. The presence of water accelerates the growth of microbe colonies which can seriously plug up a fuel system [24].

Table 2.19: Chemical and technical properties of biodiesel and diesel fuels [24].

Property	Petrodiesel	Biodiesel B100
Flash point	325 K min	410 K
Water and sediment	0.05 max %vol	0.05 max %vol
Kinematic viscosity (at 313 K)	1.3–4.1 mm^2/s	1.9–6.0 mm^2/s
Sulphated ash	–	0.02 max %wt
Ash	0.01 max %wt	–
Sulphur	0.05 max %wt	–
Sulphur	–	0.05 max %wt
Copper strip corrosion	No. 3 max	No. 3 max
Cetane number	40 min	47 min
Aromaticity	35 max %vol	–
Carbon residue	–	0.05 max %mass
Carbon residue	0.35 max %mass	–
Distillation temp (90% volume recycle)	555 K min–611 K max	–

Advantages of biodiesel

- It is renewable.
- It is energy efficient.
- It displaces petroleum-derived diesel fuel.
- It can be used in most diesel equipment with no or only minor modifications.
- It can reduce global warming gas emissions.
- It can reduce tailpipe emissions, including air toxins.
- It is non-toxic, biodegradable, and suitable for sensitive environments.
- It is made from either agricultural or recycled resources [24]

Disadvantages of biodiesel

The major disadvantages of biodiesel are its higher viscosity, lower energy content, higher cloud point and pour point, higher nitrogen oxide (NO_x) emissions, lower engine speed and power, injector coking, engine compatibility, and high price [24]

2.4.4. Biodiesel Standards

Biodiesel has become a fast growing renewable liquid biofuel. In order to ensure customer's acceptance, standardization and quality assurance are key factors for the market introduction of biodiesel as fuel for transport and heating. There are different standards for biodiesel quality. The two most well-known are EN 14214 and ASTM D6751. EN 14214 is for European Biodiesel Standard. Created by the European Committee for Standardisation, it is an international standard that describes the minimum requirements for biodiesel. ASTM D6751 details specifications for biodiesels blended with middle distillate fuels. This specification standard specifies various test methods to be used in the determination of certain properties for biodiesel blends. Biodiesels that conform to specifications for its specific grades in this standard can be run in unmodified diesel engines in the USA and Canada. A noticeable difference between those two standards for biodiesel is that EN 14214 was

designed more for B100 fuel and ASTM D6751 was developed with B20 or lower blends. ASTM D6751 includes some EN tests because they have not developed a standard for that component such as Oxidation Stability and Sodium/Potassium [31].

Table 2.20: European Standard (EN 14214) requirements for biodiesel [24].

Property	**Units**	**Lower limit**	**Upper limit**	**Test-method**
Ester content	% (m/m)	96.5	–	Pr EN 14103 d
Density at 15 °C	kg/m^3	860	900	EN ISO 3675 EN ISO 12185
Viscosity at 40 °C	mm^2/s	3.5	5.0	EN ISO 3104
Flash point	°C	>101	–	ISO CD 3679e
Sulfur content	mg/kg	–	10	–
Tar remnant (at 10% distillation remnant)	% (m/m)	–	0.3	EN ISO 10370
Cetane Lumber	–	51.0	–	EN ISO 5165
Sulfated ash content	% (m/m)	–	0.02	ISO 3987
Water content	mg/kg	–	500	EN ISO 12937
Total contamination	mg/kg	–	24	EN 12662
Copper band corrosion (3 h at 50 °C)	rating	Class 1	Class 1	EN ISO 2160
Oxidation stability at 110 °C	hours	6	-	pr EN 14112 k
Acid value	mg KOH/g	–	0.5	pr EN 14104
Iodine value	–	–	120	pr EN 14111
Linoleic acid metil ester	% (m/m)	–	12	pr EN 14103d
Polyunsaturated (4 double bonds) methylester	% (m/m)	–	1	–
Methanol content	% (m/m)	–	0.2	pr EN 141101
Monoglyceride content	% (m/m)	–	0.8	pr EN 14105m
Diglyceride content	% (m/m)	–	0.2	pr EN 14105m

Table 2.20: European Standard (EN 14214) requirements for biodiesel [24]. (continued)

Property	Units	Lower limit	Upper limit	Test-method
Triglyceride content	% (m/m)	–	0.2	pr EN 14105m
Free glycerine	% (m/m)	–	0.02	pr EN 14105m pr EN 14106
Total glycerine	% (m/m)	–	0.25	pr EN 14105m
Alkali metals (Na + K)	mg/kg	–	5	pr EN 14108 pr EN 14109
Phosphorus content	mg/kg	–	10	pr EN14107p

2.4.5. Storage of Biodiesel

One of the main criteria for the quality of a biofuel is its storage stability. Storage stability of a liquid fuel is defined by how well it resists physical and chemical changes brought about by interaction with its environment. Fuel stability may be affected by interactions of olefins, dienes and nitrogen-, sulphur-, and oxygen-containing compounds that can lead to sediment formation and changes in colour depending upon type and quantity of unstable materials present [46].

Some of the properties of biodiesel that are influenced by its storage and can provoke different problems on its stability such as oxidative degradation or microbial toxicity are:

- Free fatty acid
- Low temperature fluidity
- Water content
- Total and free glycerine
- Metal content

- Free fatty acid

Fats and oils are composed of moleculess called triglycerides. Each triglyceride is composed of three long-chain fatty acids of 8 to 24 carbons attached to a glycerol backbone. Biodiesel is composed of fatty acid chains that are chemically bonded to one methanol molecule. The glycerol molecules are almost completely removed from the final biodiesel product. When the fatty acid chains break off the triglyceride, they are known as free fatty acids. Free fatty acids are desirable biodesel feedstocks, but require different conversion processes compared to triglycerides [47].

Biodiesel typically contains up to 14 different types of fatty acids that are chemically transformed into fatty acid methyl esters (FAME). Different fractions of each type of FAME present in various feedstocks influence some of the properties of the fuel [47].

Table 2.21: Structural formula for fatty acids used in biodiesel [48].

Fatty Acid Name	**No. Of Carbons & Double Bonds**	Chemical Structure
Caprylic	C8:0	$CH_3(CH_2)_6COOH$
Capric	C10:0	$CH_3(CH_2)_8COOH$
Lauric	C12:0	$CH_3(CH_2)_{10}COOH$
Myristic	C14:0	$CH_3(CH_2)_{12}COOH$
Palmitic	C16:0	$CH_3(CH_2)_{14}COOH$
Palmitoleic	C16:1	$CH_3(CH_2)_5CH=CH(CH_2)_7COOH$
Stearic	C18:0	$CH_3(CH_2)_{16}COOH$
Oleic	C18:1	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$
Linoleic	C18:2	$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$
Linolenic	C18:3	CH3(CH2)2CH=CHCH2CH=CHCH2CH=CH(CH2)7COOH
Arachidic	C20:0	$CH_3(CH_2)_{18}COOH$
Eicosenoic	C20:1	$CH_3(CH_2)_7CH=CH(CH_2)_9COOH$
Behenic	C22:0	$CH_3(CH_2)_{20}COOH$
Eurcic	C22:1	$CH_3(CH_2)_7CH=CH(CH_2)_{11}COOH$

Table 2.22: Fatty acid compositions (wt.%) of vegetable oils [48]

Fatty acid		Palm	Olive	Peanut	Rape	Soybean	Sunflower	Lard	Tallow	Corn	Cottonseed
Caprylic	C8:0	-	-	-	-	-	-	-	-	-	-
Capric	C10:0	-	-	-	-	-	-	-	-	-	-
Lauric	C12:0	0.1	-	-	-	-	-	-	0.2	-	-
Myristic	C14:0	0.7	-	0.1	-	-	-	1.0	3.0	-	2.0
Palmitic	C16:0	36.7	11.6	8.0	4.9	11.3	6.2	27.5	27.0	6.5	20.0
Palmitoleic	C16:1	0.1	1.0	-	-	0.1	0.1	3.5	2.0	0.6	-
Stearic	C18:0	6.6	3.2	1.8	1.6	3.6	3.7	14.0	23.5	1.4	33.0
Oleic	C18:1	46.1	75.0	53.3	33.0	24.9	25.2	46.0	40.5	65.6	42.0
Linoleic	C18:2	8.6	7.8	28.4	20.4	53.0	63.1	4.8	2.0	25.2	-
Linolenic	C18:3	0.3	0.6	0.3	7.9	6.1	0.2	-	-	0.1	-
Arachidic	C20:0	0.4	0.3	0.9	-	0.3	0.3	-	0.4	0.1	-
Eicosenoic	C20:1	0.2	-	2.4	9.3	0.3	0.2	1.0	0.1	0.1	1.0
Behenic	C22:0	0.1	0.1	3.0	-	-	0.7	-	0.6	-	-
Eurcic	C22:1	-	-	-	23.0	0.3	0.1	2.0	0.2	0.1	2.0
Lignoceric	C24:0	0.1	0.5	1.8	-	0.1	0.2	0.2	0.5	-	-

Table 2.23: Saturation (wt.%) of the vegetable oils [48].

	Palm	Olive	Peanut	Rape	Soybean	Sunflower	Lard	Tallow	Corn	Cottonseed
Saturated	44.7	15.7	15.6	6.5	15.3	11.1	42.7	55.2	8.0	55.0
Monounsaturated	46.4	76.0	55.7	65.3	25.6	25.6	42.5	42.8	66.4	45.0
Polyunsaturated	8.9	8.4	28.7	28.3	59.1	63.3	4.8	2.0	25.3	-

- Low temperature fluidity

Biodiesels generally have poorer winter operability compared with straight diesel. Fuels contain wax molecules that are dissolved at higher temperatures but which crystallise out as temperatures drop [49].

Previous studies concerning the cold properties of biodiesel have determined that the length of the hydrocarbon chains and the presence of unsaturation greatly affect low temperature flow properties. The longer the carbon chains in the biodiesel, the worse the low-temperature properties. Low temperature properties depend mostly on the saturated ester content and the effect of unsaturated ester composition can be considered negligible. Unsaturated compounds act essentially as solvents, in which the saturated esters are dissolved and form which they precipitate by effect of the temperature. Biodiesel from vegetable oils such as soybean oil has better fluidity in cold climates than that from animal fat because soybean oil biodiesel has more unsaturated components [48, 49].

The cloud point, which usually occurs at a higher temperature than the pour point, is the temperature at which a liquid fatty material becomes cloudy due to the formation of crystals and solidification of saturates. Crystallization of the saturated fatty acid methyl ester components of biodiesel during cold seasons causes fuel starvation and operability problems as solidified material clog fuel lines and filters. With decreasing

temperature more solids form and material approaches the pour point, the lowest temperature at which it will cease to flow. It has been well established that the presence of higher amount of saturated components increases the cloud point and pour point of biodiesel [50].

Some of the solutions are the utilization of heaters, additives and blending biodiesel with a fuel like kerosene. The chemical additives are the most convenient and economical way of improving the low temperature properties of diesel fuels. They are generally referred to as pour point depressants, flow improvers or wax modifiers [50].

- Water content

Biodiesel can run into storage problems due to water. Biodiesel is very hydroscopic and picks up water very rapidly, and it's a delightful feedstock for microbes, so it's much more susceptible to microbial contamination. The microbes produce a gelatinous mess that is water dispersible and can plug filters and corrode pieces of equipment [51]. The presence of water in biofuels also reduces the calorific value and increases the probability that oxidation products are formed during long-term storage. Additionally, water cleaves the ester bond of the FAMEs via hydrolytic degradation [52].

- Total and free glycerine

One of the most important quality test for biodiesel is the measure of glycerine content. The key reaction in biodiesel production, transesterification, involves converting oils and fats to fatty acid methyl esters. Glycerine is the major by-product and is higher in density and more polar than the FAME. Glycerine may be present in free or bound (mono, di and triglycerides) form. Measurement of both is necessary to determine how the conversion reaction proceeded. For producers, high free glycerine content indicates poor separation, and high glycerides indicate that the reaction has not proceeded to completion or the catalyst concentration is low. For distributors and end-users high glycerine may separate out in storage, plugging pumps and filters. It can also contribute to dirty injectors or the formation of deposits on nozzles, pistons, and valves causing poor combustion conditions [52].

- Metal content

Trace metal analysis is an important part of quality control as well as quality checks of the finished products

Phosphorus

Phosphorus has been shown to damage the ability of after-treatment systems to reduce exhaust emissions as intended. The influence of phosphorus is cumulative; as a result, very low levels of contamination over the significant amount of fuel consumed by an engine can lead to unexpected deterioration of the after-treatment system [53].

Alkali and alkaline metals

Sodium and potassium hydroxides are utilized as catalysts, and magnesium and calcium as absorbents in the production of biodiesel and should be removed through the biodiesel production process. These residual metals can form deposits in fuel injection system components and poison emission control after-treatment systems [53].

Sulphur

Sulphur levels in fuel are regulated by various governmental agencies to assure compatibility with emission standard requirements. Biodiesel blends must not exceed the applicable maximum sulphur levels as defined for petroleum diesel [53].

- Oxidative degradation

Oxidative degradation is the process in which exposure to oxygen cause changes in the oil. Biodiesel is more susceptible to oxidation or autoxidation during long-term storage than conventional petrodiesel.

Due to the chemical structure of biodiesel the presence of the double bound in the molecule produce a high level of reactivity with the oxygen, especially when it placed in contact with air. Consequently, storage of biodiesel over extended periods may lead to degradation of fuel properties that can compromise fuel quality [54].

Reaction

In oxidative instability, the methylene carbons between the olefinic carbons are the sites of first attack. After hydrogen is removed from such carbons oxygen rapidly attacks and a hydroperoxide is ultimately formed where the polyunsaturation has been isomerized to include a conjugated diene. This reaction is a chain mechanism that can proceed rapidly once an initial induction period has occurred. The greater the level of unsaturation in a fatty oil or ester, the more susceptible it will be to oxidation. The rate of oxidation depends on the number and position of allylic methylene moieties (adjacent to the double bound) on the backbone of olefinic compounds. Thus, polyunsaturated esters are significantly more vulnerable to autoxidation than monounsaturated esters because they contain more allylic methylene positions. Once the hydroperoxides have formed, they decompose and inter-react to form numerous secondary oxidation products including aldehydes, alcohols, shorter chain carboxylic acids, and higher molecular weight oligomers often called polymers which can clog fuel lines, filters and pumps. Therefore, especially engine and injection pump producers insisted on the parameter oxidation stability which was finally fixed at a minimum limit of a 6-h induction period at a 110 ºC [55].

Rancimat method

The method adopted for determination of the oxidation stability is called Rancimat method and is commonly used in the vegetable oil sector. The Rancimat method mimics the oxidation of a biodiesel sample at a fixed temperature, usually far above ambient. The result is then extrapolated to the stability under storage temperature. In practice, a stream of purified air is passed through the heated sample (usually 110 ºC or 230 ºF) and is subsequently bubbled through a vessel containing deionized water [31].

The resulting oxidation products—volatile organic acids, predominantly formic acid—are swept from the sample into the water, thus increasing its continually monitored conductivity. The point at which the maximum change of the oxidation rate occurs is the induction time [31].

Many synthetic antioxidants have been investigated and used in fatty oils and esters. The most effective ones include tertiary butylhydroquinone (TBHQ), pyrogallol (PY), and propyl gallate (PG). Effective concentrations appear to be usually within the range of 200 ppm to 1000 ppm, depending on the substrate and the type of stability test used to evaluate additive performance [31].

Principal causes of oxidation

Metals, water, air, free fatty acids, high temperature, acidic fuel additives, and the presence of natural antioxidants can all impact the oxidative stability of fatty oils and esters. Oxidation can also be catalyzed by light, but such photo-oxidation should not be a significant factor for the manufacture and transportation of biodiesel fuel.

Antioxidants

For over 80 years antioxidants have either been used or proposed for use to control fatty oil oxidation. Two types of antioxidants are known: chain breakers and hydroperoxide decomposers. The phenolic compounds that have been used in fatty oils and esters are examples of chain breaking antioxidants. Crude fatty oils contain naturally occurring phenolic antioxidants, tocopherols. Tocopherols occur in four isomers: α, β, γ, and δ. The amount and distribution of these four tocopherols are a distinct characteristic of each fatty oil. Intentional use of additional amounts of tocopherols in fatty oils often provides no further benefit and sometimes decreases stability. When present in fatty oils, the γ and δ isomers appear to be the most effective antioxidants. Also, γ-tocopherol appears to be more oxidatively stable than α- tocopherol. However, when used in fatty oils and esters, tocopherols have consistently been shown to be much less effective antioxidants than synthetic antioxidants [56].

2.5. Spain and Turkey's biodiesel profile

2.5.1. Spain

The Spanish biofuels industry is composed of two main sectors: bioethanol and biodiesel production. The first biodiesel plant came into production in 2002 with a capacity of 6000 t/y. In 2007 Spain was the sixth producer in EU-27 with 168000 t, as shown in Table 2.24. Most of biodiesel consumption in Spain is in different blends:

- B2 – B5 (2-5 % Biodiesel + 95-98 % No:2 Diesel fuel) (additive)
- B20 (20 % Biodiesel + 80 % No:2 Diesel fuel) (blend component)
- B100 (100 % Biodiesel) **(** pure-neat fuel) [44].

New plant projects announced to reach more than 7 Mton production in the next years, but most of them are now closing due to the economical crisis and the fact that they can not compete with the market of United States, which their government helps the biofuels producers with subsidies of as much as 300 $ per tonne of biodiesel produced. In Spain the price of producing biodiesel is about 850 €/tone (0.75€/L), while United States can set the selling price in the Spanish market in 750 €/tonne (0.66 €/L) because of the subsidies that they get. In only 12 months United States covered 50% of the total market of biodiesel in Spain in 2007 despite the fact that Spain counted on 22 plants of production of this biofuel. For this and other reasons, a new policy is necessary in Spain, in order to have a competitive market. [44]

Some of the perspectives for the next years are:

- Extend Tax exemption period (first 10 years of the biofuel plant).
- National obligations for biofuels blending.
- Support measures to the national rural sector, fully developping possibilities supporting energetic crops.
- Subsidies and loans for producers.

Table 2.24: Production of biodiesel of the main producer countries of EU-27 in 2007 [14].

Country	**Production 2007 (Thousand of tonnes)**
Austria	267
Belgium	166
Bulgaria	9
Czech Republic	61
Denmark	85
Finland	39
France	872
Germany	2890
Greece	100
Hungary	7
Italy	363
Netherlands	85
Poland	80
Portugal	175
Slovakia	46
Spain	168
Sweden	63
UK	150
TOTAL	**5713**

2.5.2. Turkey

Biodiesel production amounted to 10.2 billion liters in 2007 and biodiesel is the most important biofuel in the EU representing almost 80 percent of biofuel consumption. EU biodiesel production was in 2007 5.7 million tonnes. This heavy concentration in the EU is primarily the result of public support for sustainable energy policies and associated regulatory initiatives that drive the development of biofuels. For example, the EU aims to increase the proportion of biofuels (whether bioethanol or biodiesel) to 5.75% of all petrol and diesel used in transport by 2010 and to 20% by 2020. (Similar growth incentives are seen as coming via regulation in the US and China.) Since the current share of biofuels in primary energy supply in the EU is approximately 3%, the European market needs to double in just 3 years in order to meet these targets. Moreover, limited land availability in the EU27 will mean that in all likelihood biodiesel will need to be imported from outside the EU27. This will favor neighboring countries such as Turkey and the Ukraine, in particular [45].

In anticipation of these growing demands in the EU as well as its own entry into the EU, Turkey has modified its laws to permit the sale and use of biofuels. The legal situation of biodiesel in Turkey can be summarized as follows. Biodiesel has been defined as the third engine fuel of the liquid fuel sector after gasoline and diesel, and it is subject to all same legal definitions, regulations, and supervision as gasoline and diesel. Biodiesel that is used for heating is subject to the same legal regulations as fuel oil and furnace fuel. Auto-biodiesel must be produced in accordance with the standard TS EN 14214, and biodiesel for heating fuel must be in accordance with the standard TS EN 14213. Auto-biodiesel can be blended at a maximum of five percent with diesel fuel according to the standard TS 3082 (EN 590). Biodiesel has become popular in Turkey since 2000. As of November 2008 there are 58 plants that have a biodiesel processing license [79]. Development of the knowledge base and production capacity in Turkey for biodiesel production represents a huge opportunity, both for Turkish domestic consumption as well as for technology and product exports to the EU and elsewhere [45]. Turkey's biodiesel production in 2007 along with the main producer countries is shown in Table 2.25.

Table 2.25: Biodiesel production of the main producer countries of the World [4, 45].

Country or Region	**Production 2007 (Million of Tonnes)**
Turkey	5.7
Spain	0.17
USA	1.2
Germany	2.9
EU	5.7
World	**15**

2.6. Literature review

M. Canakci and J. Van Gerpen (1999) investigated the effect of process variables on acid-catalyzed transesterification. The molar ratio of alcohol, reaction temperature, catalyst amount, reaction time, water content, and free fatty acids were investigated to determine the best strategy for producing biodiesel. Food grade soybean oil was used to prepare esters using excess methanol and sulfuric acid as a catalyst.

A. Demirbas (2003) reviewed the practicability of use of vegetable oils and their methyl and ethyl esters as biodiesel in compression ignition engines.

Zhang et al. (2003) designed and simulated four different continuous processes for biodiesel production from virgin oil or waste cooking oil using alkaline or acidic catalysts via a designed tool of HYSYS for the simulation of the flow rates and the chemicals involved.

M. Canakci and J. Van Gerpen (2003) constructed a pilot plant to produce biodiesel from a wide variety of feedstocks including those with high free fatty acids. A 190 L batch pilot plant had been built that can process high free fatty acid feedstocks using an acid–catalyzed pretreatment followed by an alkaline–catalyzed transesterification.

A. Bouaid et al. (2005) studied the procees of biodiesel production for pilot plant using Brassica Carinata oil as raw material with methanol and using potassium hydroxide as a calalyst.

J. Van Gerpen (2005) described the processing and production of biodiesel. He emphasized the processing in the United States, where most biodiesel is produced by reacting soybean oil or used cooking oil with methanol.

Nelson et al. (1994) evaluated the economic feasibility of a plant producing approximately 100.000 tonne/year of biodiesel. Beef tallow was transesterified with methanol in the presence of an alkali catalyst.

Noordam and Withers (1996) carried out an economic study on a biodiesel plant with a capacity of 7.800 tonne/year of biodiesel. Canola seed was used as the raw material.

Bender (1999) compared seven biodiesel plants using different oilseeds and animal fats as the raw material. The capital cost and break-even price of biodiesel for each process were determined.

Zhang et al. (2003) assessed the economic feasibilities of four different continuous processes for biodiesel production from virgin oil or waste cooking oil using alkaline or acidic catalysts via a designed tool of HYSYS for the simulation of the flow rates and the chemicals involved. They analyzed a plant of biodiesel with a capacity of 8.000 tonne/year.

M. Canakci and J. Van Gerpen (2003) estimated the costs of biodiesel using different feedstocks of a pilot plant that they constructed.

M. P. Dorado et al. (2005) made an approach to the economic of two vegetable oil-based biofuels in Spain. Used frying olive oil and non used Ethipian mustard oil were the raw material for an alkali transesterification process.

M. J. Haas et al. (2005) developed a computer model to estimate the capital and operating costs of a moderately-sized industrial biodiesel production facility. The major process operations in the plant were continuous-process vegetable oil transesterification, and ester and glycerol recovery. Crude, degummed soybean oil was specified as the feedstock.

You et al. (2007) analyzed and assessed the economic costs of three biodiesel plants with capacities of 8.000, 30.000, and 100.000 tonne/year. The plants employed

continuous processes using an alkali catalyst and the raw material of soybean oil.

J.M.N. van Kasteren and A.P. Nisworo (2007) studied the supercritical transesterification process for biodiesel continuous production from waste cooking oil for three plant capacities (125.000, 80.000, and 8.000 tonne/year).

The capital cost, manufacturing cost and the price of biodiesel were determined in each of these studies. The results for one plant from seven of these nine analysis are provided in Table 2.26.

Table **2.26:** Economic evaluations for several biodiesel production plants.

	Nelson et al. (1994)	Noordam Withers (1996)	Bender (1999)	Zhang et al. (2003)	Haas et al. (2005)	You et al. (2007)	Kasteren Nisworo (2007)
Plant capacity	100000 T/year	7800 T/year	10560 T/year	8000 T/year	33000 T/year	8000 T/year	8000 T/year
Process type	Alkali-catalyzed	Alkali-catalyzed	Alkali-catalyzed	Alkali-catalyzed	Alkali-catalyzed	Alkali-catalyzed	Supercritical transesterif.
Raw material	Beef tallow	Canola oilseed	Animal fats	Waste cooking oil	Degummed soybean oil	Degummed soybean oil	Waste cooking oil
Total fixed capital cost	$12 million	Not reported	$3.12 million	$1.34 million	$11.348 million	$1.35 million	$2 million
Total manufacturing cost	$34 million	$5.95 million	Not reported	$6.86 million	$ 21.33 million	$6.58 million	$6 million
Biodiesel break even price	$340/ tonne	$763/ tonne	$420/ tonne	$857/ tonne	$606/ tonne	$822/ tonne	$623/ tonne

3. EXPERIMENTAL PART

3. 1. Biodiesel plant process production

A plant for producing biodiesel includes reactors, distillation columns, extraction columns, heat exchangers, pumps, vessels and separators as main processing units. The process studied is an alkali-catalyzed using canola oil, a variety of rapeseed oil, as raw material and NaOH as catalyst. This process is based in the study of Zhang et al. (2003) and adapted for the economic assessment of biodiesel plants in Spain and Turkey. Process flowsheet along with the properties of main streams is presented in Fig. 3.1, and Tables 3.3 and 3.4.

- Transesterification

The reaction occurs with a 6:1 molar ratio of methanol to oil and around 1% sodium hydroxide (based on oil). Quantities for each input were calculated according to this ratio in the reaction of transesterification. As it is shown on Figure 3.1, fresh methanol (stream A at 119 kg/h), recycled methanol (stream L at 97,6 kg/h) and anhydrous sodium hydroxide (stream B at 11.4 kg/h) are mixed before being pumped into reactor R-1 by pump P-1. Degummed and neutralized canola oil (stream F at 1000 kg/h) is heated in exchanger E-1 before entering R-1 [58]. Alcohol, catalyst and oil are combined in reactor R-1 and agitated for approximately 1 h at 60 ºC and 400 kPa. Smaller plants often use batch reactors, but most larger plants use continuous flow processes involving continuous stirred-tank reactors (CSTR) or plug flow reactors [59]. The conversion of oil to FAME in this first reactor is 94.6%. Also in R-1 glycerol is produced as a by-product.

- Methanol recovery

In C-1, five theoretical stages and a reflux ratio of 2 are used to obtain a good separation between methanol and other components. Vacuum distillation is used to keep the bottom temperature under 150 ºC [58]. Pure methanol is recovered in stream

K, containing 94.2% of the total methanol in stream J, and then is mixed with the fresh methanol for being charged back into reactor R-1. Stream M is cooled in exchanger E-2 to 60 ºC and sent to washing column W-1.

- Water washing

A water washing column W-1 with four theoretical steps is used to carry out the complete separation [58]. In this step FAME is separated from glycerol, methanol and catalyst by adding 10 kg/h of water at 25 ºC. The amounts of unconverted oil, methanol and water in stream Q are small, just 6.1%, and FAME is the rest. All of the glycerol remains in the bottom stream R, containing 84.1% glycerol, and the rest is water, methanol and sodium hydroxide.

- FAME purification

Stream Q is forwarded to C-2 distillation column, which has four theoretical stages and a reflux ratio of 2. This column operates under vacuum to keep temperatures low enough to prevent degradation of the FAME. A partial condenser is used to provide easy separation of the FAME from water and methanol in the column overhead and superheated high pressure steam is the heating medium for the reboiler [58]. FAME product is obtained as a liquid distillate product in stream X (957 kg/h at 195 ºC and 10 kPa) with a purity of 99.7% (enough pure for ASTM specifications). Unconverted oil at stream Y (55 kg/h) is treated as a waste because is a small amount. Water and methanol are removed as vent gases (stream AA).

- Alkali removal and glycerine purification

A neutralization reactor R-2 removes sodium hydroxide from stream R (118.4 kg/h) by adding 8.5 kg/h of phosphoric acid (stream S). Then, a gravity separator X-1 removes the resulting Na_3PO_4 (stream W).

Stream V free of alkali (113 kg/h and glycerol purity of 88.1%) is fed into purification column C-3, which operates with four theoretical stages and a reflux ratio of 2, in order to reach a higher grade of glycerine. In this column water and methanol are removed in distillate stream AB (5 kg/h) and glycerine is obtained as a high quality by-product at the bottom stream Z (107.8 kg/h and 92.4% pure) [58].

Table 3.1 summarizes the input and output quantities of the main substances of the process and their properties. Table 3.2 present some specifications of the process studied.

Table 3.1: Molecular weight, density and input and ouput mass flow of the main substances of the process [20].

Substance	**Molecular weight**	**Density**	**Input / output amounts**
Canola oil (TG)	886 kg/kmol	0.899 kg/L	1000 kg/h
MeOH	32 kg/kmol	0.791 kg/L	216 kg/h
NaOH	40 kg/kmol	2.100 kg/L	11.4 kg/h
H_3PO_4	98 kg/kmol	1.685 kg/L	8.5 kg/h
Glycerol	92 kg/kmol	1.261 kg/L	99.6 kg/h
Biodiesel (FAME)	888 kg/kmol	0.874 kg/L	957 kg/h
Na_3PO_4	165 kg/kmol	1.620 kg/L	13.4 kg/h

Table 3.2: Biodiesel process specifications.

Plant capacity	8000 t/year biodiesel
Methanol recovery	94.2 %
FAME purity	99.7 wt. %

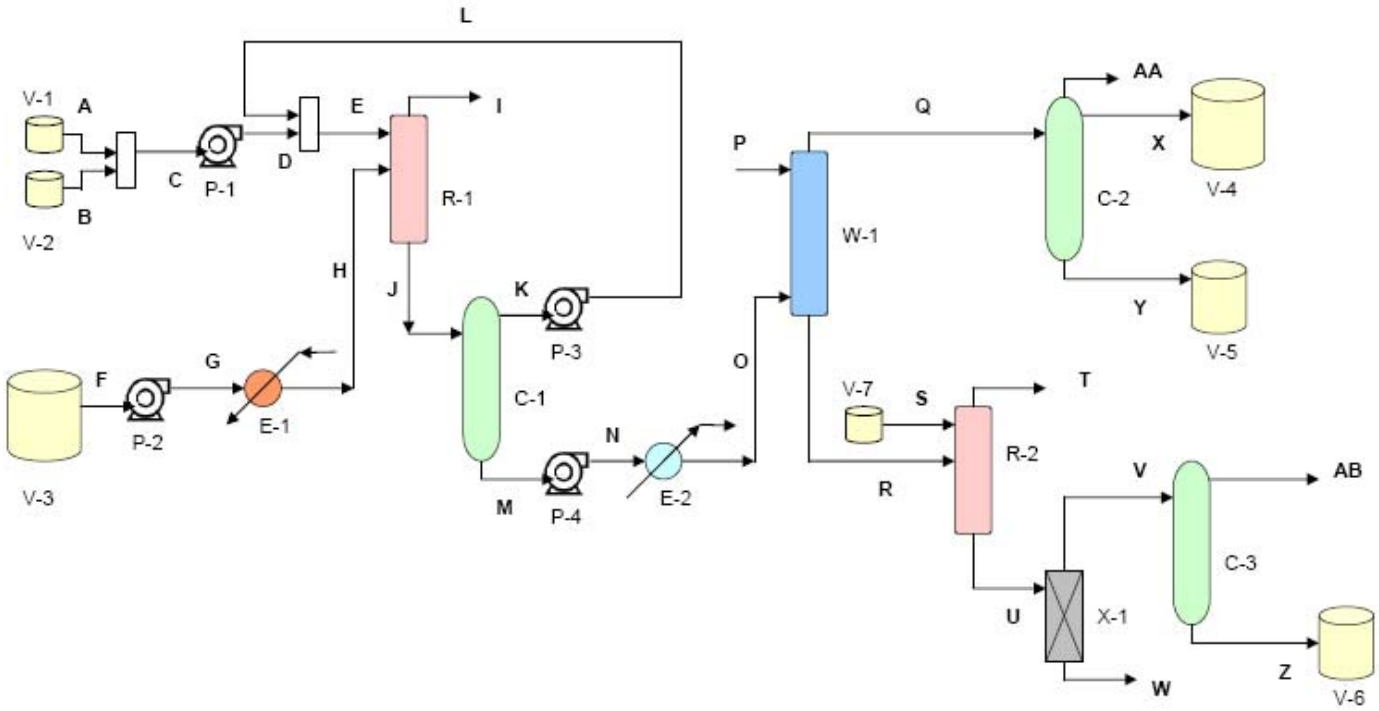

Figure 3.1. Flowsheet of biodiesel production process [58].

Code	Element
R-1	Transesterification reactor
R-2	Neutralization reactor
C-1	MeOH distillation
C-2	FAME distillation
C-3	Glycerol purification
W-1	Washing column
V-1	MeOH storage vessel
V-2	NaOH storage vessel
V-3	Canola oil storage vessel
V-4	FAME storage vessel
V-5	Oil (waste) storage vessel
V-6	Glycerol storage vessel
V-7	H_3PO_4 storage vessel
P-1	MeOH – NaOH pump
P-2	Oil pump
P-3	MeOH recovery head pump
P-4	MeOH recovery bottom pump
E-1	Heat exchanger (heather)
E-2	Heat exchanger (cooling)
X-1	Gravity separator

Table 3.3: Mass balance of biodiesel production process. Component mass fracion [58].

Stream name	**A**	**B**	**E**	**H**	**J**	**L**	**M**	**P**	**Q**	**R**	**S**	**U**	**V**	**W**	**X**	**Y**	**Z**	**AA**	**AB**
Temp (ºC)	25	25	27	60	60	28	122	25	60	60	25	60	60	60	195	415	110	195	55
Pressure (kPa)	100	100	400	400	400	400	30	100	110	110	110	110	110	110	10	20	50	10	40
Mass flow (kg/h)	119	11.4	228	1000	1228	9,6	1130	10	1022	118.4	8.5	126.9	113	13.9	960	55	107.8	7	5
Component mass fraction																			
Methanol	1.000		0.950		0.084	1.000	0.005		0.003	0.025		0.024	0.027					0.429	0.600
Canola oil					0.045		0.049		0.054							1.000			
FAME					0.782		0.849		0.939						0.997			0.429	
Glycerol					0.081		0.088			0.841		0.785	0.881				0.924		
NaOH		1.000	0.050		0.008		0.009			0.083									
H_2O								1.000	0.004	0.049		0.080	0.090		0.003		0.076	0.143	0.400
H_3PO_4											1.000	0.004		0.036					
Na_3PO_4												0.106		0.964					

Table 3.4: Mass balance of biodiesel production process. Component mass flow. [58]

Stream name	A	B	E	H	J	L	M	P	Q	R	S	U	V	W	X	Y	Z	AA	AB
Temp (ºC)	25	25	27	60	60	28	122	25	60	60	25	60	60	60	195	415	110	195	55
Pressure (kPa)	100	100	400	400	400	400	30	100	110	110	110	110	110	110	10	20	50	10	40
Mass flow (kg/h)	119	11.4	228	1000	1228	97.6	1130	10	1022	118.4	8.5	126.9	113	13.9	960	55	107.8	7	5
Component mass flow (kg/h)																			
Methanol	119		216.6		103.6	97.6	6		3	3		3	3					3	3
Canola oil				1000	55		55		55							55			
FAME					960		960		960						957			3	
Glycerol					99.6		99.6			99.6		99.6	99.6				99.6		
NaOH		11.4	11.4		9.8		9.8			9.8									
H_2O								10	4	5.8		10.2	10.2		3		8.2	1	2
H_3PO_4											8.5	0.5		0.5					
Na_3PO_4												13.4		13.4					

3. 2. Biodiesel plant economic assessment

3. 2. 1. Basis and scope of calculations

First of all, the following process assumptions were stablished:

- The production capacity was 8000 tonne/year biodiesel.
- Operating hours for the biodiesel plant were assumed to be 8400 h/year.
- Canola oil, used as the feedstock for biodiesel production is free of water and any solid impurities.
- Density of canola oil and biodiesel were assumed to be 0.899 kg/L and 0.874 kg/L respectively.
- Pressure drop of the process equipments is neglected.
- Superheated, low and higher pressure streams were used as the heating media. Water was the cooling medium.
- Some equipment prices (reactors, columns, heat exchangers and separator) were updated from mid-2000 to 2008 values using Chemical Engineering Plant Cost Index, where I_{2000} = 394.1 and I_{2008} = 549.2 [58, 60].
- The rest of the equipment prices (pumps and vessels) were calculated using CEPCI values from mid-1982 to 2008, where I_{1982} = 315 and I_{2008} = 549.2 [60, 61].
- All costs are given in Euro €.
- The range of expected accurancy of the following study is between +30% and -20% [62].

The first step after these assumptions was to set up the prices for every chemical product and utility used in the current process for both countries Spain and Turkey. Prices for chemicals and utilities are shown in Table 3.5 and 3.6, respectively.

Table 3.5: Prices of the raw materials, catalyst and products.

Chemicals	**Price €/Tm (Spain)**	**Price €/Tm (Turkey)**
Biodiesel	750 [64]	1060 [68]
Glycerine 92 wt. %	775 [65]	530 [69]
Methanol	220 [66]	250 [70]
Phosphoric acid	1100 [66]	850 [71]
Sodium hydroxide	430 [66]	250 [72]
Canola oil (degummed and neutralized)	590 [67]	920 [73]

Table 3.6: Prices of the utilities used in the process. [63, 74, 75]

Utilities	**Price (Spain)**	**Price (Turkey)**
Cooling water	6.56 €/GJ	6.56 €/GJ
Electricity	0.061 €/kWh	0.066 €/kWh
HP steam	5.83 €/GJ	5.83 €/GJ
MP steam	4.37 €/GJ	4.37 €/GJ
Waste treatment	0.002 €/kg	0.002 €/kg

After determining the prices of the chemicals and utilities involved in the process, the equipment cost along with the capital cost was estimated. The procedure of the economic assessment used in this study is the same that Gael D. Ulrich presented in 1984, and nowadays it is still a tool of calculations for many chemical engineers.

Equipment sizing was based on the study of Zhang et al. (2003) except storage vessels, which were assumed to have one month of storage capacity. Results for sizing the main equipment of the process, equipment costs and fixed capital costs are shown in Table 3.7.

Table 3.7: Equipment sizes, equipment costs and fixed capital costs [61,63].

Equipment Identification	Code	Capacity / Size	Equipment cost (1982 or 2000)	CEPCI coefficient	Equipment cost (2008)	Total ($x10^{-3}$)	
Reactors							
Transesterification	R-1	L= 5.4 m , D= 1.8 m	290000	1.508	404234	$ 434	€ 334
Neutralization	R-2	L= 1.0 m , D= 0.3 m	21000	1.508	29272		
Columns							
MeOH distillation	C-1	H= 10 m , D= 0.6 m	140000	1.508	195147		
FAME distillation	C-2	H= 12 m, D= 1.2 m	157000	1.508	218844	$ 700	€ 538
Glycerol purification	C-3	H= 10 m, D= 0.5 m	106000	1.508	147754		
Washing column	W-1	H= 10 m, D= 0.8 m	100000	1.508	139391		
Storage Vessels							
MeOH	V-1	V= 101 m^3	7500	1.886	63664		
NaOH	V-2	V= 4 m^3	1500	1.886	12733		
Canola oil (TG)	V-3	V= 748 m^3	23000	1.886	195237	$ 558	€ 429
FAME	V-4	V= 738 m^3	22000	1.886	186749		
Oil (waste)	V-5	V= 41 m^3	4800	1.886	40745		
Glycerol	V-6	V= 58 m^3	5500	1.886	46687		
H_3PO_4	V-7	V= 3 m^3	1400	1.886	11884		

Table 3.7: Equipment sizes, equipment costs and fixed capital costs (continued) [61,63].

Equipment Identification	Code	Capacity / Size	Equipment cost (1982 or 2000)	CEPCI coefficient	Equipment cost (2008)	Total ($x10^{-3}$)	
Pumps							
MeOH – NaOH	P-1	W_S= 0.016 kW	5850	1.886	11035		
Oil	P-2	W_S= 0.015 kW	5400	1.886	10186	$ 46	€ 35
MeOH recovery head	P-3	W_S= 0.016 kW	6300	1.886	11884		
MeOH recovery bottom	P-4	W_S= 0.067 kW	6750	1.886	12733		
Heat exchangers	E-1/E-2	H= 67.2 / 164.5 MJ/h	4000	1.508	6032	$ 6	€ 5
Separators	X-1	-	46000	1.508	64120	$ 64	€ 49
Total bare module						$ 1808	€ 1390
Contingency and fee					$ 1808k x 0.18	$ 325	€ 250
Total module cost						$ 2133	€ 1640
Auxiliary facilities					$ 2133k x 0.30	$ 640	€ 495
Grass-roots capital						$ 2773	€ 2135

In the current study, fixed capital cost, total manufacturing cost, after-tax rate of return and break-even price of biodiesel in both cases Spain and Turkey are evaluated. Prices per year and prices per kg of biodiesel are presented in Table 3.8 and 3.9. All of these calculations follow the steps and rules described in the guide writen by Ulrich, 1984.

- Fixed capital cost, or grass-roots capital cost, represents the cost of constructing a new plant. Generally, fixed capital cost consists of three parts: bare module capital cost, contingencies and fees, and costs associated with auxiliary facilities. Fixed capital cost along with its three parts is presented in Table 3.8 and 3.9.

    - Total bare module capital cost is the sum of the cost of each piece of the equipment in the process.

    - Contingencies and fees are defined as a fraction of the total bare module capital cost to cover unforeseen circumstances and contractor fees. In this work 18% was used.

    - Expenses and auxiliary facilities include items such as the purchase of land, installation of electrical and water systems and construction of all internal roads. They are usually represented by 30% of the total basic module cost (sum of total bare module capital cost and contingencies and fees) [63].

- Total capital investment is calculated by adding the fixed capital cost to the working capital cost. Working capital cost is usually a fraction of the fixed capital cost (15% in the present study). Total capital investment is shown in Table 3.8 and 3.9.

- Total manufacturing cost refers to the cost of the day-to-day operation of achemical plant and is usually divided into three categories: direct manufacturing costs, indirect or fixed manufacturing costs and general expenses. Total manufacturing cost and its three categories are shown in Table 3.8 and 3.9.

- Direct manufacturing costs consist of raw material and catalyst cost, operating labor fees, supervisory and clerical labor fees, utilities (including waste disposal), manteinance and repairs, operating supplies, laboratory charges, and expenses for patents and royalties.

  - Raw materials, catalyst and utilities costs were calculated based on the price of each chemical presented in Table 3.5 and 3.6, and their flowrate and usage [63].

  - The operator labor fee was estimated according to the indications of Ulrich, 1984. It was assumed that an operator works 50 weeks/year and there were three turns a day for a continuosly running plant. Operator salary was estimated at 20 €/h.

  - The rest of the expenses were calculated by multiplying by related factors.

- Indirect manufacturing costs include overhead, packaging, storage, local taxes, insurance and depreciation. All of the items in this category are independent of the production rate in a plant.

- General expenses includes administrative costs, distribution and selling costs, and research and development charges. Similarly, items pertaining to indirect manufacturing costs and general expenses were also computed and multiplied by various constant factors, which are commonly applied to economic assesments and are shown in Table 3.8 and 3.9 [63].

- After-tax rate of return is a general economic performance criteria for the preliminar evaluation of a chemical plant and is defined as the percentage of net annual profit after taxes relative to the total capital investment. Net annual profit after taxes (A_{NNP}) is equal to income after taxes (A_{IT}) and is the half of the net annual profit (A_{NP}) when a 50% corporate tax rate is used. After-tax rate of return is also presented in Table 3.8 and 3.9 [64].

- Break-even price is defined as the price for which revenue from biodiesel product is the same as total manufacturing cost of a plant [64].

Table 3.8: Total manufacturing costs and after-tax rate of return for Spain [61, 63].

Fixed capital, C_{FC}	2135000 €	
Working capital (15% of C_{FC})	320250 €	
Total capital investment, C_{TC}	2455250 €	
	€/year (x 10^{-3})	€/kg
Manufacturing expenses		
Direct		
Raw materials		
Oil feedstock	5000	0.625
Methanol	220	0.028
NaOH	42	0.005
H_3PO_4	80	0.010
Operating labour, C_{OL}	300	0.038
Supervisory and clerical labour (15% of C_{OL})	45	0.006
Utilities		
HP Steam	26	0.003
MP Steam	3	0.000
Electricity	18	0.002
Cooling water	50	0.006
Waste disposal	5	0.001
Maintenance and repairs (6% of C_{FC}), C_{MR}	128	0.016
Operating supplies (15% of C_{MR})	19	0.002
Laboratory charges (15% of C_{OL})	45	0.006
Patents and royalties (3% of A_{TE})	21	0.003

Table 3.8: Total manufacturing costs and after-tax rate of return for Spain (continued) [61, 63].

Total, A_{DME}	6002	0.750
Indirect		
Overhead, packaging, storage (60% of the sum of C_{OL}, supervision and maintenance)	180	0.023
Local taxes (1,5% of C_{FC})	32	0.004
Insurance (0,7% of C_{FC})	15	0.002
Total, A_{IME}	227	0.028
Depreciation (10% of C_{FC}), A_{BD}	214	0.027
General expenses		
Administrative costs (25% of overhead)	45	0.006
Distribution and selling costs (10% of A_{TE})	685	0.086
Research and development (5% of A_{TE})	343	0.043
Total, A_{GE}	1073	0.134
Total production cost	7500	0.938
Glycerine credit	650	0.081
Total expense, A_{TE}	6850	0.856
Revenue from biodiesel	6030	0.754
Net annual profit, A_{NP}	- 820	- 0.102
Income taxes (50% of A_{NP}), A_{IT}	- 410	- 0.051
Net annual profit after taxes (A_{NP} - A_{IT}), A_{NNP}	- 410	- 0.051
After-tax rate of return, I = [A_{NNP} + A_{BD}] / C_{TC}, (%)	- 25.4	-

Table 3.9: Total manufacturing costs and after-tax rate of return for Turkey [61, 63].

Fixed capital, C_{FC}	2135000 €	
Working capital (15% of C_{FC})	320250 €	
Total capital investment, C_{TC}	2455250 €	
	10^3 €/year	€/kg
Manufacturing expenses		
Direct		
Raw materials		
Oil feedstock	7730	0.966
Methanol	250	0.031
NaOH	24	0.003
H_3PO_4	60	0.008
Operating labour, C_{OL}	230	0.029
Supervisory and clerical labour (15% of C_{OL})	45	0.006
Utilities		
HP Steam	26	0.003
MP Steam	3	0.000
Electricity	20	0.003
Cooling water	50	0.006
Waste disposal	5	0.001
Maintenance and repairs (6% of C_{FC}), C_{MR}	128	0.016
Operating supplies (15% of C_{MR})	19	0.002
Laboratory charges (15% of C_{OL})	45	0.006
Patents and royalties (3% of A_{TE})	317	0.039
Total, A_{DME}	8952	1.119

Table 3.9: Total manufacturing costs and after-tax rate of return for Turkey (continued) [61, 63].

Indirect		
Overhead, packaging, storage (60% of the sum of C_{OL}, supervision and maintenance)	180	0.023
Local taxes (1,5% of C_{FC})	32	0.004
Insurance (0,7% of C_{FC})	15	0.002
Total, A_{IME}	227	0.028
Depreciation (10% of C_{FC}), A_{BD}	214	0.027
General expenses		
Administrative costs (25% of overhead)	45	0.006
Distribution and selling costs (10% of A_{TE})	1058	0.132
Research and development (5% of A_{TE})	529	0.066
Total, A_{GE}	1632	0.204
Total production cost	10135	1.267
Glycerine credit	445	0.055
Total expense, A_{TE}	10580	1.322
Revenue from biodiesel	8.480	1.060
Net annual profit, A_{NP}	-2100	-0.263
Income taxes (50% of A_{NP}), A_{IT}	-1050	-0.132
Net annual profit after taxes (A_{NP} - A_{IT}), A_{NNP}	-1050	-0.132
Aftertax rate of return, I = [A_{NNP} + A_{BD}] / C_{TC}, (%)	-51.5	-

4. RESULTS AND DISCUSSIONS

Two biodiesel production plants were considered, one in Spain and the other one in Turkey. The values of fixed capital cost, total manufacturing cost, after-tax rate of return and break-even price were determined for both of them in the previous section.

- Fixed capital cost

In the two cases the fixed capital cost is identical because the equipment cost for both countries Spain and Turkey was assumed to be the same. As shown in Table 3.7, the element that is most signifiant of the fixed capital cost is the transesterification reactor (almost 15% of capital cost), followed by the columns, storage vessels and separators. A detailed comparison of my results with those of others can not be done, because the plant capacity along with the year of the study are different. Table 2.26 presents the fixed capital cost of the previous studies. The studies of Zhang et al. and You et al. can be compared due to the fact that the plant capacity is the same as that one in the present work, but only if the prices are updated to the year 2008. The work of Kasteren and Nisworo could be compared if the process was alkaly-catalized like the rest of the studies. The fixed capital cost in this study is 2135000 €, and the updated costs for the plant of Zhang et al. and You et al. are 2020000 € aproximately. Thus, the capital cost of this study seems reasonable.

- Total manufacturing cost

The total manufacturing cost of the two plants is different due to the fact that the costs of raw materials, employer's salary and utilities are not the same in the studied countries. Tables 3.8 and 3.9 shows those quantities. In both cases, the direct costs are the highest ones, being 6002000 € for Spain (93% of total maufacturing) and 8952000 € for Turkey (95% of total manufacturing). There is a big difference between them, and it is

mainly because of the price of the canola oil, which comprises 83% and 86% of the total direct costs, and 78% and 82% of the total manufacturing costs, for the Spanish and Turkish plants, respectively. The total cost of raw material in one year is 5342000 € for Spain (83% of total manufacturing), and 8064000 € for Turkey (86% of total manufacturing). Thus, the raw material price comprises almost the same share of the total manufacturing cost than the direct costs. In comparison to the previous studies, this cost can be considered reliable in the case of the Spanish plant, because it is very similar. The cost for the Turkish plant can also be considered reasonable since the main cause of this high value is the price of canola oil, that is quite expensive in this country. Table 2.26 presents a comparison of the total manufacturing cost of the previous studies.

- After-tax rate of return and break-even price

In both cases the annual profit is negative, being -820000 € for the Spanish plant, and -2100000 € for the Turkish one, and also the after-tax rate of return (after-tax rate of loss). This means that the process is not profitable and some financial help would be required, as government subsidies. The after-tax rate of loss amounts to 25.4% and 51.5% of the total capital investment, for the processes in Spain and Turkey, respectively. The production process in Spain appears to be more economical because of the lower price of the canola oil, basically. Consequently, some government subsidies are needed, mainly in Turkey, as USA. does, as well as a reduction of the price of canola oil to make biodiesel profitable, Table 3.8 and 3.9 show the annual profit and after-tax rate of return of each production plant.

The break-even price of biodiesel for the plant in Spain in this study is 856 €/tonne, and 1322 €/tonne for the Turkish one. In comparison to the previous studies, the price of one tonne of biodiesel produced in Spain is higher but in Turkey is much higher. Table 2.26 presents the break-even price of biodiesel for the previous studies, in $. The biodiesel produced in US.A. is still cheaper than that produced in Spain or Turkey (the selling price is about 600 €), which is due to the subsidies that the producers receive from the government. If in Spain a subsidy existed, the biodiesel would be competitive in that country, and USA. would not be the leader of the Spanish market.

Table 4.1 shows a summary of economic assessment results in order to compare and contrast the two production plants of biodiesel studied in the present work.

Table 4.1: Summary of economic assessment results of the Spanish and Turkish biodiesel plants.

	Biodiesel plant in Spain	Biodiesel plant in Turkey
Plant capacity	8000 T/year	8000 T/year
Process type	Alkali-catalyzed	Alkali-catalyzed
Raw material	Canola oil (degummed & neutralized)	Canola oil (degummed & neutralized)
Total fixed capital cost	2.14 million €	2.14 million €
Total manufacturing cost	6.4 million €	9.4 million €
Biodiesel break even price	856 €/tonne	1322 €/tonne

5. CONCLUSIONS

According to the economic assessment of two biodiesel plants, one in Spain and the other one in Turkey, producing biodiesel with a continuous alkali-catalyzed process using canola oil as the raw material, the following conclusions were made:

- Canola oil cost account for a major portion of the total manufacturing cost, in both cases Spain and Turkey, being higher in the last one. For that reason, reduction of this raw material cost should be the first step in optimizing the total manufacturing cost.

- Glycerine is a valuable by-product, which can contribute in the reduction of the total manufacturing cost by 5-9% for a plant with 8000 T/year biodiesel capacity. A higher purity of glycerine (85-92% wt.) means that the credit for that by-product is also higher.

- Based on after-tax rate of return and break-even price, the Spanish process appears to be economically competitive, but a reduction on the biodiesel price is required since the Spanish biodiesel is not the most consumed in Spain currently. This reduction would be a fact with the new policies stablished by the government.

- The Turkish process is not economically profitable, and the main cause is the high cost of the oil feedstock. First of all, a cheaper raw material is needed, and then some government subsidies would help to make biodiesel affordable in Turkey.

Some solutions could be found to make these two processess profitable. For example new feedstocks, as algae, with bigger amount of oil content and cheaper price. The problem is that the technology to process this feedstock is different from the rest of the traditional ones, and another equipment is needed. A few new plants in Spain are begining to run with algae as a feedstock for biodiesel. Some recent studies in the Centre of Excellence for Hazardous Materials Management in Nuevo Mexico, USA, synthesized a variety of algae capable to produce 50% of oil, the half part of their weight. The calculations made from some experts are that the market of algae is profitable at least with a production of 25% of oil from that feedstock [76]. Moreover, in Spain, the governmet decided to support in June 2009 the investigation of algae with 12 million of euros, with a construction of a National Bank of Algae and four photo-bioreactors. This project is also stood by some well-known companies as Repsol, Acciona, Endesa and Abengoa [77]. Also, in June 2009, it was presented in Florence the European Algae Biomass Association, to promote the algae as a suitable feedstock for biofuels, pharmacist and chemical products and animal food [78].

Another feedstock could be the recycled frying oil from restaurants. The price is lower than the virgin oils and the technology is almost the same, just a pre-treatment, basically a esterification reactor and a liquid extraction column, is needed to reduce the content of free fatty acids in the oil. In that process the capital investment is higher due to the necessity of more equipment, but the price of the raw material is three times lower that virgin oils. According to the study of Zhang et al. (2003), biodiesel from waste cooking oil results cheaper just if the process is an acid-catalyzed [58, 63].

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